



Comprehensive Isotopic Analyses of Sources, Flow Paths, and Geochemical Processes Affecting Nitrate in Central Coast Groundwater

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Executive Summary

The Central Coast Regional Water Quality Control Board (Central Coast Water Board, CCWB) is responsible for protecting water quality and the beneficial uses of surface water and groundwater in the Central Coast Region. Many of the groundwater basins in the region are impaired by nitrate contamination. The objective of this study is to evaluate groundwater residence times, nitrate sources, and geochemical processes affecting nitrate concentrations in groundwater basins within the Central Coast Region. New laboratory analyses of isotopic tracers, dissolved gas concentrations, and nutrient concentrations were conducted for this study and compiled with existing groundwater quality and isotopic data from prior studies, to address the following research questions:

- *What is the status of nitrate concentrations in Central Coast groundwater basins?*

Nitrate concentrations are above the Maximum Contaminant Level (MCL, 10 mg NO₃-N per liter) in 29% of all groundwater samples in Central Coast groundwater basins. The proportions vary between Santa Maria Valley (35%), Salinas Valley (25%), and Gilroy-Hollister Valley (29%). The majority of these data are from the CCWB's Irrigated Lands Program monitoring efforts collected mainly between 2012 and 2017, with additional data from GAMA Priority Basin, GAMA Shallow Aquifer Assessment projects. (See Table 5. Nitrate concentrations in Central Coast groundwater basins)

- *How does groundwater age vary spatially and with depth?*

Groundwater ages were calculated from ³H/³He isotope ratios to study the history of nitrate loading to groundwater. Forty six percent of groundwater samples were “modern”, i.e. they had recharged since the 1950s and contained tritium but no evidence for fossil water. For these samples, a ³H/³He age was calculated. Twenty percent of samples were identified as fossil groundwater, recharged over a thousand years ago. An additional 19% of samples were a mixture between modern recharge and fossil water. Fifteen percent of samples had recharged entirely before 1950 (contained no detectable tritium and no ³H/³He could be calculated), but they also had no evidence of fossil water. (See Table 7. Groundwater age classification)

Groundwater age generally increases with depth below the water table (Figure 10). The age-depth gradient is spatially variable with high gradients in Santa Maria Valley and moderate gradients in the central part of Salinas Valley (Figure 11). Low age gradients were found in the upper Salinas Valley.

- *What are the present-day sources of nitrate loading to groundwater?*

Detailed data on Total Nitrogen Applied on agricultural land, reported by growers to the Irrigated Lands Program in 2018, were analyzed to evaluate the contribution of different sources to the present-day soil nitrogen budget. Fertilizer is the most prevalent source of nitrogen (63%) applied to agricultural lands. Fertilizer nitrogen is cycled through soil organic matter by microbial interactions or by plant uptake and subsequent composting of biomass. Fertilizer nitrogen has accumulated in agricultural soils and is available to plants at high concentrations, contributing 14% to the soil nitrogen budget. Nitrate in pumped groundwater used for irrigation is another important source of nitrogen to agricultural lands (22%). Where the total nitrogen application is above 1000 lbs/acre, this

source can contribute up to 40% of total N applied. (See *Table 6. Nitrogen available to crops*)

- *Which sources of nitrate are identified in groundwater?*

Analysis of oxygen and nitrogen isotopes in groundwater nitrate can provide an indication of the original source of nitrogen leaching. However, biogeochemical cycling of nitrogen in soils often resets the nitrate isotopic signature before leaching to groundwater. Nitrate isotopes identify a direct fertilizer source of groundwater nitrate in six samples and a direct contribution of ammonia or urea fertilizer to groundwater nitrate in six samples. Two samples probably have a septic or manure source. (See *Figure 5: Measured nitrate isotopic signatures compared to potential sources*)

- *What is the history of nitrate loading to groundwater?*

The proportion of wells with nitrate concentrations above the MCL is between 12% and 40% for all age categories except fossil groundwater. Differences between modern groundwater age categories recharged since the 1950s are not significant. This indicates that high nitrate concentrations have leached into groundwater starting before the 1950s and continued into the 2000s. Long well screens—over 50% of wells in this dataset have a screen length greater than 100 ft—cause mixing of groundwater flow paths and limit the ability to detect trends in response to changes in land management practices. (See *Figure 12: Proportion of samples with nitrate concentrations above the MCL within each age category*)

- *What are the sources of recharge in Central Coast groundwater basins and what is the impact on nitrate concentrations?*

Low $\delta^{18}\text{O}$ values and low noble gas recharge temperatures (NGRT) in groundwater on the eastern side of Santa Maria Valley indicate that river water is a source of recharge to the basin. (See *Figure 13: Interpolated maps of $\delta^{18}\text{O}$ and noble gas recharge temperature show the extent of river water recharge in the eastern portion of Santa Maria Valley.*) Clear patterns in $\delta^{18}\text{O}$ or NGRT are not found in the Salinas Valley or Gilroy-Hollister Valley.

Nitrate concentrations are lower in groundwater with a river water recharge source than in groundwater recharged by local precipitation or groundwater-irrigation return flow. (See *Figure 14: Nitrate concentrations with respect to $\delta^{18}\text{O}$ -H₂O and noble gas recharge temperatures in Santa Maria Valley.*) While river water recharge results in lower nitrate concentrations, 35% of wells still contain nitrate in excess of the MCL in areas of river water recharge as opposed to 70% in the remainder of Santa Maria Valley.

- *Does denitrification protect groundwater resources from nitrate concentrations exceeding the MCL of 10 mg NO₃-N per liter?*

Without denitrification occurring in soils and groundwater, nitrate concentrations would exceed the MCL in more wells. We estimate that in 16% of all wells, the nitrate concentration is below the MCL because of denitrification. Nitrate concentrations still exceed the MCL in 29% of all samples.

- *Are high nitrate wells different from other wells in terms of (1) nitrogen source, (2) flow paths, and (3) geochemical processes?*

Based on the dataset compiled for this study, wells with nitrate concentrations above the MCL have (1) higher N application rates from fertilizer, soil and irrigation, (2) higher vertical age gradients and shallower groundwater tables, (3) a smaller component of river recharge and a larger contribution of natural precipitation or irrigation recharge, and (4) higher dissolved oxygen concentrations and less denitrification. (See *Table 12. t-test of explanatory variables.*)

1 Nitrate in Central Coast Groundwater

1.1 Study Objectives

The Central Coast Regional Water Quality Control Board (Central Coast Water Board, CCWB) is responsible for protecting water quality and the beneficial uses of surface water and groundwater in the Central Coast Region. Many of the groundwater basins in the region are impaired by nitrate contamination. The CCWB, via the Central Coast Ambient Monitoring Program – Groundwater Assessment and Protection Program (CCAMP-GAP), seeks to understand the source, fate, and transport of nitrate within a few of the most impaired groundwater basins in the Central Coast Region. Specifically, CCWB wants to understand the sources and history of nitrogen loading contributing to high nitrate concentrations observed in groundwater. CCWB partnered with LLNL to carry out a study of nitrate sources and occurrence using geochemical and isotopic tracers. The objective of this study is to evaluate groundwater residence times, nitrate sources, and geochemical processes affecting nitrate concentrations in groundwater basins within the Central Coast Region using a variety of isotopic tracer and age-dating analytical methods (e.g., nitrogen and oxygen isotopes of nitrate, $^3\text{H}/^3\text{He}$ groundwater age).

The study is focused on three valleys within the CCWB region: Santa Maria Valley, Salinas Valley, and Gilroy-Hollister Valley. Results are aggregated for these three areas and differences are examined.

This study addresses the following questions:

- *What is the status of nitrate concentrations in Central Coast groundwater basins?*
- *How does groundwater age vary spatially and with depth?*
- *What are the present-day sources of nitrate loading to groundwater?*
- *Which sources of nitrate are identified in groundwater?)*
- *What is the history of nitrate loading to groundwater?*
- *What are the sources of recharge in Central Coast groundwater basins and what is the impact on nitrate concentrations?*
- *Does denitrification protect groundwater resources from nitrate concentrations exceeding the MCL of 10 mg $\text{NO}_3\text{-N}$ per liter?*
- *Are high nitrate wells different from other wells in terms of (1) nitrogen source, (2) flow paths, and (3) geochemical processes?*

1.2 Approach

For this study, new laboratory analyses (performed at LLNL) of groundwater samples (newly collected by CCWB) were combined with existing datasets of groundwater quality (e.g., CCWB Irrigated Lands Program) and isotopic data from prior studies (conducted by LLNL or the USGS). The research questions formulated above were addressed based on a comprehensive review of the integrated dataset. New laboratory analyses included a suite of isotopic tracers, dissolved gas concentrations, and nutrient concentrations. Groundwater ages were calculated

based on $^3\text{H}/^3\text{He}$ isotopic ratios to study the history of nitrate loading to groundwater. Spatial trends in vertical age gradients were used to examine the effect of groundwater flow paths on the occurrence of nitrate in wells. Recharge mechanism and sources were identified based on dissolved noble gas concentrations and stable isotopes of water to examine the effect of river water recharge on nitrate concentrations. Nitrate isotopes were examined as an indicator of the source of nitrogen to the groundwater system, and to evaluate the progress of denitrification. Denitrification was further examined using dissolved N_2 -excess concentrations. The patterns of denitrification were extrapolated using the dissolved oxygen concentration to calculate the effect of denitrification on the proportion of wells with nitrate concentrations above the MCL. Nitrogen application rates reported by growers were analyzed spatially to further evaluate nitrogen sources to groundwater. Characteristics of wells with nitrate concentrations above the MCL are summarized in a series of Student's t-tests.

2 Research Methods

2.1 Study Areas

Our study focused on three areas (Figure 1) of intensive agricultural production within the CCWB region: Santa Maria Valley (SMV), Salinas Valley (SV), and Gilroy-Hollister Valley (GHV). These areas, in particular Salinas Valley, known as ‘the salad bowl of the world’, have been agricultural centers for more than 100 years. Irrigated row crops are common forms of land use and water use in each of the valleys. The duration and intensity of this land use has led to contamination of groundwater by nitrate from fertilizers¹⁻⁴ and nitrate concentrations often exceed the MCL of 10 mg NO₃-N per liter (45 mg/L as NO₃) set by the US Environmental Protection Agency (EPA).

2.1.1 Hydrogeology

Groundwater in these areas predominantly resides in major unconsolidated sedimentary groundwater basins under unconfined, semi-confined, and confined conditions.

For this study, the Santa Maria Valley area includes samples from the following groundwater basins defined by the California Department of Water Resources (DWR): Santa Maria River Valley, Santa Ynez River Valley, San Antonio Creek Valley, and San Luis Obispo Valley. Alluvium in the Santa Maria River Valley groundwater basin consists of unconsolidated clay, silt, sand, and gravel ranging up to approximately 200 feet in thickness. The primary components of recharge in the Santa Maria River Valley groundwater basin are natural infiltration of precipitation, streamflow, irrigation return flow, and treated wastewater return flows. Contributions from stormwater infiltration ponds, infiltration of surface runoff from mountains, and septic system return flows are minor.¹⁻⁴

Located within the Coast Ranges between the San Joaquin Valley and the Pacific Ocean, the Salinas Valley groundwater basin is the largest coastal groundwater basin in Central California. For this study, the Salinas Valley area includes the Salinas Valley, Corralitos, Santa Margarita, Santa Cruz Mid-County, and the West Santa Cruz Terrace groundwater basins. Unconsolidated and semi-consolidated alluvial fan and river deposits become interbedded with marine clays in the northern portion of the Salinas Valley groundwater basin. Episodic changes in sea level during Miocene through Pleistocene times led to alternating deposition between coarse grained materials in riverine and alluvial fan environments, and fine-grained sediments in estuarine and marine environments.¹⁻⁴

For this study, the Gilroy-Hollister Valley area includes samples from the Gilroy-Hollister and Santa Clara Valley groundwater basins. Alluvial fan material from Coyote Creek, Llagas Creek and Uvas Creek forms the Gilroy-Hollister Valley groundwater basin. Alluvial sediments are more than 1000 feet thick in the southern portion of the Gilroy-Hollister Valley groundwater basin.¹⁻⁴

2.1.2 Previous Studies on Nitrate in Central Coast groundwater

Between 1993 and 2000, the U.S. Geological Survey’s National Water-Quality Assessment program found that 9% of domestic supply wells and 2% of public supply wells exceeded the Environmental Protection Agency’s MCL for drinking water.⁵

Locations of groundwater samples

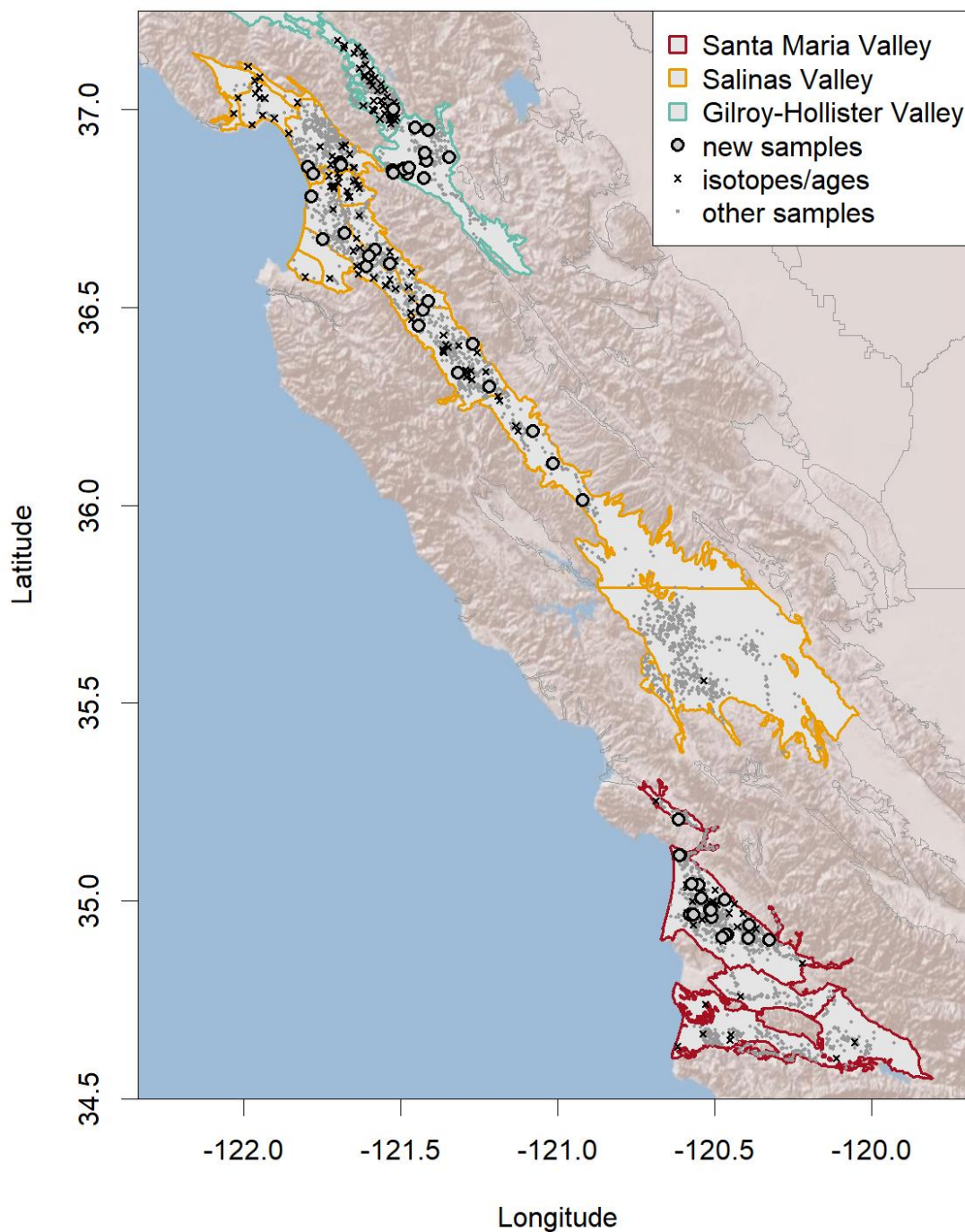


Figure 1. Locations of groundwater samples analyzed in this study.

The Groundwater Ambient Monitoring and Assessment (GAMA) Program's Monterey-Salinas Priority Basin Study found nitrate concentrations to exceed the MCL in 8% of the primary aquifers, based on a comprehensive data set of water quality and isotopic indicators from public supply wells.⁶

The State Water Board sampled 38 domestic wells within the Salinas Valley and Pajaro Valley as part of the GAMA Program Domestic Well Project⁷ and found seven wells with nitrate concentrations greater than the MCL in Salinas Valley. Additionally, stable water isotopes, nitrogen isotopes, and boron isotopes were collected at each well site. The wells that exceed the nitrate MCL had overlapping ranges of nitrate isotopic concentrations and nitrate sources could not be distinguished from nitrogen isotopes alone.

The GAMA USGS Monterey-Salinas Shallow Aquifer Study Unit⁸ found nitrate concentrations in domestic wells in the Salinas Valley to exceed the MCL in 14% of samples collected. Using a non-parametric statistical analysis to examine the relationship between nitrate and potential explanatory factors including land use, well construction, groundwater age, and geochemical conditions, this study found that nitrate concentrations over the MCL were generally associated with shallow wells (less than 350 feet) and groundwater that had a modern age or a mixture of pre-modern and modern water.

A UC Davis study⁹ for the State Water Resources Control Board found that the majority of the public supply wells in the Salinas Valley have concentrations below the MCL. Because public supply wells are subject to Monterey County Health Department regulations, when the MCL of a particular contaminant is exceeded, public wells are often abandoned, or use is discontinued and there is no further sampling. This causes a sampling bias because the majority of wells sampled are below the MCL. The study also found that the higher average nitrate concentrations were located in wells in the northeastern, central, and southern portions of the Salinas Valley.

The Central Coast Groundwater Coalition (CCGC) was formed to meet groundwater monitoring requirements of the Central Coast Regional Water Quality Control Board's (Regional Water Board's) Conditional Waiver of Waste Discharge Requirements for Discharges from Irrigated Lands (adopted Order No. R3-2012-0011) and associated Monitoring and Reporting Programs (MRPs).¹ Data generated by CCGC from on-farm domestic well monitoring provide information that helps with the current understanding of groundwater quality for domestic consumption throughout the region.

Based on data from its monitoring efforts, CCGC created water quality maps^{1,2} for each of the subbasins included in this study by integrating available analytical data with on-farm groundwater samples collected since 2013. CCGC found a mean nitrate concentration in groundwater of 7.7 mg NO₃-N/L (34 mg/L as NO₃) in the Santa Maria groundwater basin with 22 % of wells exceeding the MCL. The mean nitrate concentration in groundwater used for domestic supply for the entire Salinas Valley Groundwater Basin was 15 mg NO₃-N/L (68 mg/L as NO₃). A total of 309 wells (41 %) had maximum concentrations above over the MCL throughout the Salinas Valley. There are large areas in the East Side Subbasin of the Salinas Valley where groundwater nitrate concentrations are mapped as greater than the MCL. The mean concentration in Gilroy-Hollister Valley was 8.1 mg NO₃-N/L (36 mg/L as NO₃). 26% of wells had maximum concentrations over the MCL. CCGC found that lower nitrate concentrations in CCGC samples were generally associated with chemically reducing conditions with oxidation-reduction potential values less than 75 mV.¹

Two prior LLNL isotopic studies were focused on nitrate in the Central Coast region, one in the Salinas Valley (conducted in 2009-2010) and one in the Llagas groundwater basin (conducted in 2003). In the Salinas Valley, geochemical and isotopic results indicate that irrigated agriculture is the largest source of nitrate to groundwater and surface water in sampled areas where nitrate concentrations are elevated above the low background concentration. Nitrate isotopic compositions, when adjusted for partial denitrification and variable degrees of isotopic enrichment, are consistent with an inorganic fertilizer source in samples with nitrate concentrations above the background level. Very low concentrations of nitrate (less than 4 mg/L as NO_3) are observed in wells adjacent to Arroyo Seco. The Arroyo Seco (a tributary to the Salinas River) served as a “background” location with respect to nitrate because land cover is predominantly natural and the river and groundwater are relatively pristine. The isotopic composition of nitrate in these samples also reflects its natural source.⁴

Monitoring well samples from the Salinas Valley show evidence of denitrification, either by isotopic compositions that are enriched in ^{15}N and ^{18}O , or by the presence of excess dissolved nitrogen. Denitrification is therefore an important process in reducing nitrate concentrations in groundwater near the Salinas River. Regional groundwater pumping for irrigation accelerates groundwater flow such that high nitrate groundwater reaches the capture zone of some drinking water wells. Which areas are affected depends upon aquifer heterogeneity and vertical transport pathways, along with pumping patterns and connections to sources of irrigation return flow.

In the Llagas basin, synthetic fertilizer is the most likely source of nitrate in highly contaminated wells. The shallow aquifer is highly vulnerable because of high vertical recharge rates. Deeper aquifers are relatively more protected by laterally extensive aquitards. Denitrification is not a significant process in the fate of nitrate (except in the area of recycled water application). The nitrate management plan for the Llagas basin¹⁰ has not yet resulted in a decrease in the flux of nitrate to the shallow aquifer in the areas tested.³

2.2 Data Compilation

For this study, CCWB staff collected new samples from groundwater wells between September 2018 and January 2019. The new samples were collected from 54 groundwater wells used for public supply or domestic drinking water in the central coast region and analyzed for nitrate concentration, isotopes of nitrogen and oxygen in nitrate, stable isotopes of hydrogen and oxygen in water, tritium, dissolved gases including nitrogen, noble gases and the helium isotope ratio. This new dataset expanded isotopic data collected in previous studies within the California State Water Resources Control Board’s (SWRCB’s) Groundwater Ambient Monitoring and Assessment (GAMA) program. These prior studies included analyses of either nitrate isotopes or groundwater age (tritium and noble gases), or in some cases, both. The GAMA Program is a comprehensive groundwater quality monitoring program managed by the SWRCB and includes the GAMA Domestic Well study⁷ conducted by UC Davis,⁹ the GAMA Special Studies in the Salinas Valley⁴ and Llagas Basin³ conducted by LLNL, and the GAMA Priority Basin⁶ and Shallow Aquifer Assessment⁸ study conducted by the USGS California Water Resources Center. The number of samples obtained from each source of data is listed in Table 1.

The dataset was further expanded by including groundwater monitoring data from irrigation and domestic supply wells submitted by growers to the Central Coast Water Board’s Irrigated Lands Program (ILP) as required by the 2012 and 2017 agricultural regulatory orders (Ag Orders).¹¹

Data from the ILP did not include nitrate isotopic or groundwater age metrics but provided additional insight into the spatial distribution of nitrate and geochemical processes.

The dataset was limited to groundwater samples collected within groundwater basins defined by DWR. The number of nitrate and isotopic analyses included in this study for each area and groundwater basin are summarized in Table 2. Due to the differences in the designs and objectives of the studies that generated these datasets, a limited number of samples had a complete set of chemical, isotopic, and groundwater age tracer data.

The wells included in this study are mostly domestic, irrigation, or public supply wells. Over 90% of the wells have a total depth of more than 100 ft, and 32% have a total depth of over 500 ft. The well screen is more than 100 ft long in 53% of the wells, and more than 200 ft in 32% of the wells. Groundwater samples collected from long well screens are more likely to contain a mixture of ages and flow paths, and a nitrate concentration that is the average of all contributing flow paths. The wells represent the groundwater presently used for domestic, irrigation or public supply, but they are not ideal to detect trends in groundwater quality or the impact of nutrient management plans.

Table 1. Number of samples included in the data analysis

	Source	Santa Maria Valley	Salinas Valley	Gilroy-Hollister Valley	Total
Color code					
Total number of samples	This study	18	22	14	54
	LLNL studies	0	41	56	97
	GAMA studies	74	276	11	361
	ILP	2154	3203	681	6038
	Total	2246	3542	762	6550
Number of samples with isotope data	This study	18	22	14	54
	LLNL studies	0	33	54	87
	GAMA studies	34	91	1	126
	Total	52	146	69	267

Table 2. Number of samples with isotopic data in each of the groundwater basins included in this study.

Area	Samples	Groundwater Basin	DWR Basin Code
Santa Maria Valley	2	SAN LUIS OBISPO VALLEY	3-009
Santa Maria Valley	41	SANTA MARIA RIVER VALLEY	3-012
Santa Maria Valley	1	SAN ANTONIO CREEK VALLEY	3-014
Santa Maria Valley	8	SANTA YNEZ RIVER VALLEY	3-015
Salinas Valley	10	SANTA CRUZ MID-COUNTY	3-001
Salinas Valley	20	CORRALITOS	3-002
Salinas Valley	113	SALINAS VALLEY	3-004
Salinas Valley	2	WEST SANTA CRUZ TERRACE	3-026
Salinas Valley	1	SANTA MARGARITA	3-027
Gilroy-Hollister Valley	5	SANTA CLARA VALLEY	2-009
Gilroy-Hollister Valley	64	GILROY-HOLLISTER VALLEY	3-003

2.3 New Sample Collection and Analysis

New samples for tritium, stable isotopes of water, nitrate concentrations and isotopes, and dissolved noble gases were collected by CCWB staff in accordance with LLNL procedures. GAMA Priority Basin and Shallow Aquifer Assessment samples were collected following USGS procedures⁸. Analyses of samples collected for this study were performed at LLNL. Stable isotope ratios of nitrogen and oxygen in nitrate were analyzed using the denitrifying bacteria procedure. Denitrifying bacteria reduce nitrate to nitrous oxide gas ($\text{N}_2\text{O(g)}$) which is analyzed for $^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$ ratios on an IsoPrime isotope ratio mass spectrometer equipped with a TraceGas sample introduction system. The measured nitrogen and oxygen isotope ratios are referenced against standards and expressed as $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$. Analytical uncertainty (1σ) is 0.5‰ for $\delta^{15}\text{N-NO}_3$ and 1.0‰ for $\delta^{18}\text{O-NO}_3$. Dissolved gases for determination of excess nitrogen were measured as part of the dissolved noble gas analysis.¹² Noble gases, including the helium isotope ratio were measured on a VG5400 mass spectrometer, Ar was measured using a high-sensitivity capacitive manometer, and Ne, Kr, and Xe were measured on an SRS RGA200 quadrupole mass spectrometer by isotope dilution.¹³⁻¹⁵ Tritium was determined by way of ^3He accumulation.¹⁶ Noble gas recharge temperatures and the excess air component were based on the concentrations of Ne, Ar, Kr, and Xe. Locations and well construction information of newly collected samples are in Table 13. Results of new laboratory analyses are in Table 14 (nitrate and isotopes) and Table 15 (dissolved gases). Derived parameters (groundwater age, terrigenous helium, age category, noble gas recharge temperature, excess dissolved N_2) are in Table 16.

2.4 Data Analysis and Interpretation

2.4.1 Estimating the Proportion of Wells with Nitrate Concentrations Above the MCL

In this study we focus on the proportion of wells with nitrate concentrations above the MCL of 10 mg NO₃-N per liter. We carefully examined the dataset to avoid sampling bias in the calculation of the proportion of samples with nitrate concentrations above the MCL. In addition, we calculated the 95%-confidence intervals on the proportion¹⁷ to illustrate the uncertainty associated with calculating a proportion on a limited number of samples. To distinguish statistically significant differences between subsets of wells (e.g. the difference between the proportion of wells with nitrate above the MCL in samples that recharged either before or after the year 2000), we performed 2-sample tests for equality of proportions.¹⁸

The GAMA Priority Basin and Shallow Aquifer Assessment programs were designed to assess regional scale groundwater quality and estimate aquifer scale proportions by collecting samples from equal area grids.¹⁹ However, the focus of the Priority Basin program on public supply wells led to a bias towards wells with low concentrations of nitrate or other regulated contaminants because public supply wells are typically drilled deeper than private domestic wells and screened over longer intervals. Both greater depths and longer screens can have diluting effects on water quality results. In addition, public supply wells with concentrations of nitrate or other contaminants above the MCL are often abandoned, inactive, or destroyed. Therefore, the Priority Basin dataset may have underestimated the extent of the nitrate problem in the Central Coast region. The Shallow Aquifer Assessment program dataset included private domestic wells, which are not regulated in California, and better represents the status of groundwater quality in groundwater basins. The focus of the ILP groundwater monitoring requirements was to assess nitrate impacts to groundwater in agricultural areas and samples were collected from on-farm irrigation and domestic supply wells. Newly collected samples within the scope of this study also focused on areas of intensive agriculture, with multiple crop rotations per year, little to no fallowing, and cultivation of crops that require large amounts of nitrogen. Because data included in this study was retrieved from multiple sources with different objectives, the analysis and interpretation of the comprehensive dataset is focused on understanding trends between nitrate and geochemical, isotopic, or groundwater age metrics.

2.4.2 Sources of Nitrogen to Groundwater Nitrate

Four different sources of nitrogen contribute to nitrate leaching below the root zone: fertilizer in various forms, soil nitrification, nitrate in groundwater used for irrigation, and compost. Since 2014, specific growers in the central coast have reported the contributions of these four sources to the Central Coast Water Board in accordance with prior and existing Ag Orders. We use these data to examine how nitrate sources may contribute to nitrate leaching since 2014. Prior studies have examined historical nitrogen applications from county-level fertilizer sales.²⁰⁻²³ Additionally, we examined nitrate isotopes in groundwater samples as a possible technique to identify nitrogen sources to nitrate leaching.

2.4.2.1 Nitrate Isotopes

Nitrate isotopes are analyzed to identify sources of nitrogen and evaluate the effect of denitrification on nitrate concentrations. Five external sources of nitrogen in groundwater are commonly considered: Nitrogen from precipitation, as nitrate or ammonium; natural nitrogen

fixation in soils; septic systems; organic fertilizer; and synthetic fertilizer applied as nitrate, ammonium, or urea. Soil nitrogen exists in the form of soil organic matter (SOM) and as mineral nitrogen (nitrate, ammonium, or nitrous oxides). Molecular nitrogen (N_2) in soils is considered inert and not included in the discussion.

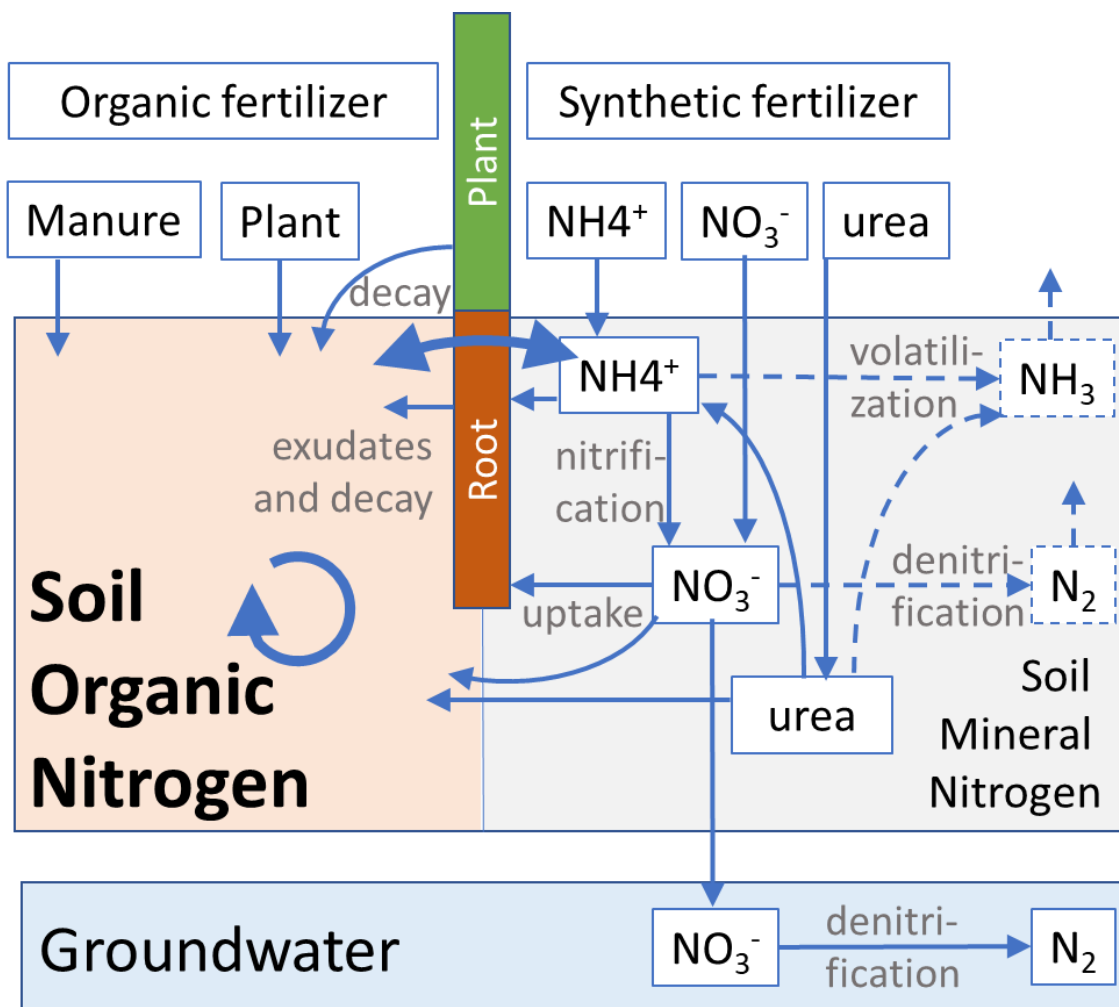


Figure 2. Schematic of nitrogen cycle.

Biological soil processes transfer nitrogen between soil nitrogen pools (Figure 2). Each transformation can lead to fractionation of nitrogen isotopes. The degree of fractionation depends on soil conditions and the rate and extent of the transformation. As a result, different pools of nitrogen in the soil have very variable nitrogen isotopic ratios. There are no predictive models available that reliably incorporate all processes and associated fractionation because enrichment factors and soil conditions are not adequately known. Therefore, the definition of ^{15}N pools in soils and groundwater is based on a compilation of measurements in a growing number of studies (Table 3). The first compilation of studies with measurements of ^{15}N and ^{18}O in nitrogen sources was published by Kendall.²⁴ A recent review by Nikolenko²⁵ included more studies and resulted in similar ranges of values. A study by Bateman²⁶ focused on nitrate isotope signatures in fertilizer.

$\delta^{15}\text{N}$ values reported for synthetic fertilizer sources (NH_4 and NO_3), which are derived from nitrogen from the atmosphere, range from -9.5 to +7 ‰ (Table 3).^{24, 25} A recent study including 153 measurements found a mean $\delta^{15}\text{N}$ of 0.2 ‰ with a standard deviation (sd) of 1.6 ‰. 80% of measurements were within 2 ‰ of zero.²⁶ Small differences in nitrogen isotopes in nitrate fertilizer (0.0 ‰), ammonium fertilizer (3.3 ‰) and urea fertilizer (-1.1 ‰) have been observed.²⁷ However, the effect of fractionating processes on the nitrogen isotopic composition of nitrate that originated as synthetic fertilizer are expected to be larger than these differences.

$\delta^{15}\text{N}$ of soil nitrogen varies between 3 and 8 ‰ according to the compilations by Kendall and Nikolenko. The distributions of $\delta^{15}\text{N}$ in natural soils (mean: 3.9 ‰; sd: 3.9‰) and fertilized soils (mean: 3.5 ‰; sd: 3.9 ‰) reported by Kendall are similar. Recent field studies²⁸⁻³¹ report pre-treatment soil nitrogen isotope ratios for bulk soil (5.1 - 8.9 ‰), organic nitrogen (6.8 - 7.7 ‰) and soil nitrate (6.5 - 10.0 ‰). These are at the high end of the typically reported range. Nitrate $\delta^{15}\text{N}$ is similar or slightly higher than soil nitrogen.

The large range in $\delta^{15}\text{N}$ in organic fertilizer reflects the various biological processes that produce it. Manure values range from 0-35 ‰, reflecting the effects of fractionating processes such as discrimination during assimilation of nitrogen in animals, and varying degrees of ammonia volatilization.²⁴⁻²⁶ In one study,³² manure (5-7 ‰, n=4) appeared to be distinct from composted manure (9-21 ‰, n=37)

Literature references to compost often mean a composted mixture of pig manure and sawdust. The $\delta^{15}\text{N}$ value of “compost” is around 16 ‰.²⁸ Soil treatments with compost (0 to 1500 mg N per kg soil; pre-treatment soil N was 1250 mg/kg) resulted in $\delta^{15}\text{N}$ of soil nitrate of 8.3-18.4 ‰,²⁸ reflecting the range of soil N (6.8 ‰) to compost (16 ‰) and a subtle shift of +2‰. In the same experiment, harvested Chinese cabbage from these soils had $\delta^{15}\text{N}$ of 11-21 ‰, reflecting an additional shift of +3 ‰. The amount of nitrogen applied to these soils was higher than typical agricultural practices. In a more representative study,²⁹ nitrogen was applied at 150 kg N/ha in the form of urea, compost or a mixture of both. This represented an 1.3% increase of the pre-treatment soil N content of 1800 mg/kg over the top 40 cm. The addition of urea or compost did not result in a change in the soil $\delta^{15}\text{N}$. The $\delta^{15}\text{N}$ of maize closely reflected source N at 30 days but converged to soil $\delta^{15}\text{N}$ values after 70 days.

Tilling a large portion of plant material back into the soil after harvest, instead of removing it from the field, adds a substantial amount of nitrogen to the soil as organic matter. This plant material will be available for mineralization and leaching on short time-scales unless the organic matter is persistent or protected from mineralization inside soil aggregates. There are no studies available on the effect of composted plant material and tillage of crop remains on the $\delta^{15}\text{N}$ of soil or nitrate. The experimental studies described can give an idea of the expected result. Crop $\delta^{15}\text{N}$ values closely resemble soil $\delta^{15}\text{N}$ at the end of the growing season, reflecting the soil N that was taken up. Because crop $\delta^{15}\text{N}$ values resemble soil $\delta^{15}\text{N}$, tillage of crop remains into the soil is not expected to cause a shift in $\delta^{15}\text{N}$ of soil N or the nitrate leaching from the soil. The fractionation of nitrogen isotopes observed between pig manure and composted manure (often referred to in literature as “compost”) is likely the result of the conditions in the composter, where ammonia volatilization causes fractionation. These conditions are not likely in tilled soils and soil N derived from plant N will be similar to plant N in terms of $\delta^{15}\text{N}$. Because the original nitrogen for this plant material may be derived from artificial fertilizer, tilling plant material into the soil after harvest adds nitrogen to the soil with a typical “soil” signature, which can be leached after mineralization.

Table 3. Nitrate isotopes in sources compiled from several studies.

Source	Value	Rain NH ₄	Rain NO ₃	Soil	Fertilized Soil	Septic	Animal	Composted Manure	NH ₄ Fertilizer	NO ₃ Fertilizer	Fertilizer	Urea
δ¹⁵N (‰)												
Kendall ²⁴	min	-7.5	-3	2.5	2.5	0	0		-9.5	-3		
	max	5	9	8	8	25	25		3.5	3		
	mean	-4.5	0.6	3.9	3.5	10.1	13.6		-1.2	0.8		
	sd	4.2	3.5	3.9	3.9	8.2	6.9		1.4	1.5		
Nikolenko ²⁵	min ^a		-12	3		3	5			-8		
	max ^a		11	8		25	35			7		
	min ^b	-13.4		2.4		5	8		-7.4			
	max ^b	2.3		4.1		9.0	11.0		5.1			
Bateman ²⁶	mean										0.2	
	sd										1.6	
Nommik ²⁷									3.3	0	1.7	-1.1
Lim ³²	min						5	9				
	max						7	21				
Yun ²⁸				6.8				16				
Zhou ³³				5.14				11.71				
					5.27 ^c							
					7.44 ^d							
δ¹⁸O (‰)												
Kendall ²⁴	min		18							17		
	max		68							24		
Nikolenko ²⁵	min		30							17		
	max		70							25		

^a: δ¹⁵N of NO₃; ^b: δ¹⁵N of NH₄^c: fertilized with urea; ^d: fertilized with compost

The isotopic ratio of oxygen atoms in nitrate can also reflect the source and transformation processes. Synthetic nitrate fertilizer is produced from atmospheric nitrogen and oxygen and the isotopic ratios are close to atmospheric (+23.5 ‰). Nitrate produced by biological processes in soils derive oxygen from both soil air (1/3) and soil water (2/3). Soil air is assumed to have atmospheric oxygen isotope ratios, although soil respiration can fractionate soil oxygen. The ranges of oxygen isotope ratios for nitrate sources (other than rain and fertilizer) were calculated as 1/3rd the atmospheric oxygen isotope ratio and 2/3rd the range of oxygen isotope ratios of water ($\delta^{18}\text{O-H}_2\text{O}$) measured in groundwater samples in this study.

Nitrate isotopic compositions measured in groundwater will reflect the starting fertilizer isotopic composition plus transformations that occur in the soil zone. Cases where groundwater nitrate isotopes are identical to the fertilizer source involve direct leaching of fertilizer dissolved in water either bypassing the soil or overwhelming the biological soil nitrogen cycle. Nitrate isotopic composition in between typical soil nitrogen and fertilizer signatures are a clear indication that fertilizer was the original source.³⁴ A nitrate isotopic composition similar to soil nitrogen is not evidence that nitrate is natural and fertilizer has not contributed to the dissolved nitrate concentration.

Figure 3 illustrates the large ranges of nitrate isotopic values reported in these compilation studies, together with the data included in this study, in a dual isotope plot of $\delta^{18}\text{O-NO}_3$ vs $\delta^{15}\text{N-NO}_3$. Dashed boxes contain the entire range of values for each of the sources of nitrate to groundwater. Considerable overlap of the boxes, movement out of boxes during N transformations, and mixing between sources all call for an alternative method of visualization and more nuanced categorization of sources. The color intensity on the strip-charts beside the $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ axes represent the number of studies included in Kendall's compilation²⁴ reporting a value within a 2 ‰ bin. The distribution of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values for each source of N was approximated by a normal distribution. The uncertainty of the source signatures is represented by ellipses that contain 50% of the joint probability density function of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$.

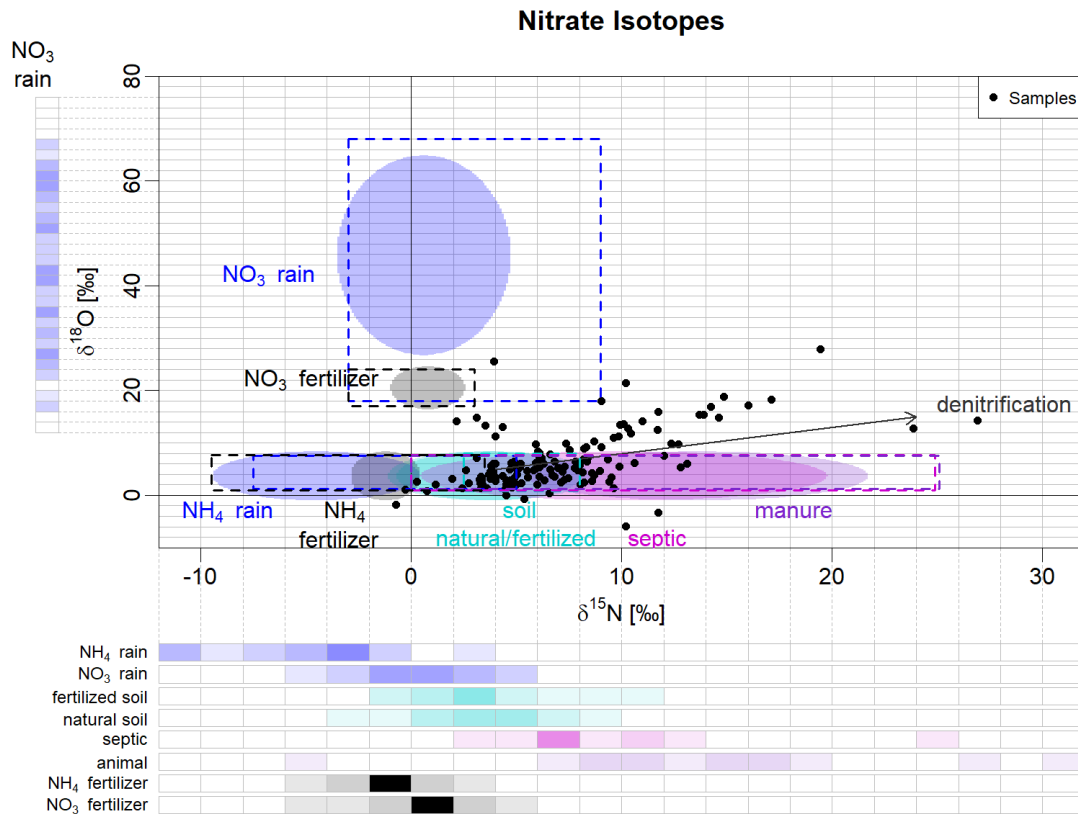


Figure 3: Potential sources of nitrogen to groundwater nitrate.

2.4.2.2 Nitrogen Source Reporting

Total crop available nitrogen is reported by growers in pounds per acre at the ranch scale. Applied fertilizer is reported for each crop grown in a single calendar year. Multiple crops can be rotated within a ranch in one year. Applied compost is reported as a total for the entire ranch area. Crop available soil nitrogen is measured and reported before fertilizer applications. Nitrate concentrations in groundwater used for irrigation are reported in combination with total irrigated water volume to estimate the amount of nitrogen applied in irrigation water. The sum of these four sources (fertilizer, compost, soil, and irrigation water) represents the total crop available nitrogen. Crop uptake and soil denitrification remove nitrogen from the soil balance before nitrate leaching occurs. Variation in crop uptake and soil nitrogen cycling, as well as soil hydrology, influence the nitrate concentration of water leaching from the root zone. While accounting for nitrogen sources to the root zone helps establish patterns of nitrogen intensity, it does not necessarily directly relate to nitrate concentrations in groundwater.

The contributions of these sources were aggregated and analyzed for each of the three study areas. A spatial analysis was performed on the nitrogen application data to identify regions where high nitrogen application rates coincide with groundwater nitrate concentrations. Such coincidences may indicate sustained practices that lead to nitrate leaching to groundwater but cannot directly attribute high nitrate concentrations in groundwater to nitrogen application rates reported for 2018 because groundwater ages can be several decades old.

2.4.3 River Water Recharge

Recharge of river water, either directly or via irrigation, can have an influence on nitrate concentrations. Direct river water recharge is expected to contain very low nitrate concentrations, especially compared to the high concentrations of nitrate often found in groundwater irrigation that contribute to the soil nitrogen balance.

River water recharge can be identified by analyzing the stable isotopes of water (e.g. $\delta^{18}\text{O}\text{-H}_2\text{O}$) or noble gas recharge temperatures.³⁵ The origin of river water in California is often higher elevation watersheds where $\delta^{18}\text{O}\text{-H}_2\text{O}$ values in precipitation are lower than valleys at lower elevation. Focused river water recharge also often occurs under lower temperatures than local precipitation recharge or irrigation return flow. We used both indicators to study the effect of river water recharge on nitrate concentrations in the Santa Maria groundwater basin.

2.4.4 $^3\text{H}/^3\text{He}$ Groundwater Ages

Groundwater age is an important metric to reconstruct nitrate loading history to groundwater. Groundwater samples collected from short-screened monitoring wells can provide detailed insight into groundwater quality trends in relation to groundwater age as well as reactive transport. Long screens and active pumping of public supply or irrigation wells on the other hand result in groundwater samples that represent a mixture of groundwater flow paths, sources, and groundwater ages. Establishing the complex groundwater age distribution in such samples is possible with a combination of groundwater age tracers³⁶⁻³⁸ or with a limited number of age tracers and a predetermined shape of the groundwater age distribution based on the regional groundwater flow system.^{39, 40} In this study, we rely on $^3\text{H}/^3\text{He}$ apparent ages as the main metric for groundwater age, which is calculated as

$$\text{age} = \ln(^3\text{He}^* / ^3\text{H} + 1) / \lambda$$

With $^3\text{He}^*$ the tritiogenic helium-3 concentration, ^3H the tritium concentration and λ the tritium decay constant (0.05626 yr^{-1}).⁴¹ In mixed groundwater samples (from long-screened pumping wells), the apparent $^3\text{H}/^3\text{He}$ age represents the age of the modern groundwater component that recharged since the introduction of tritium in the atmosphere by nuclear testing. This apparent age can be biased towards periods with high tritium concentrations in recharging groundwater, typically around the 1963 “bomb peak” of tritium in precipitation. Mixing of modern and pre-modern groundwater can be detected if the sum of tritium and tritiogenic helium (reflecting the initial concentration of tritium at the water table) does not correspond to the level of tritium in precipitation at the calculated time of recharge.

In addition to $^3\text{H}/^3\text{He}$ ages, we use the presence of terrigenous helium-4 as an indicator groundwater with an age of hundreds to thousands of years. Terrigenous helium-4 accumulates slowly in groundwater from the decay of naturally occurring uranium and thorium and by diffusion from the Earth’s crust and mantle.

Groundwater samples were characterized in different recharge periods based on the $^3\text{H}/^3\text{He}$ age, the tritium content (expressed in pico-Curies per liter, pCi/L), and the terrigenous helium-4 concentration (expressed in cubic centimeter gas at standard temperature and pressure per gram of water, $\text{cm}^3\text{STP/g}$, Table 4Table 1). If a reliable $^3\text{H}/^3\text{He}$ could be calculated with an uncertainty of less than 10 years, the year of recharge was classified in 10-year bins from 1970 to 2010. If the sample contained both tritium and terrigenous helium, the sample was considered a mixture of fossil and modern water with an undetermined age. Samples with less than 1 pCi/L tritium and

more than 5×10^{-9} cm³STP/g terrigenic helium are classified as fossil. Samples with less than 1 pCi/L tritium and less than 5×10^{-9} cm³STP/g terrigenic helium were classified Old/Unknown. Groundwater containing less than 1 pCi/L is normally considered pre-modern. However, in our study, this category included samples with a clear impact of recent anthropogenic influence. This can be attributed to mixing of pre-modern (tritium-free) groundwater with recent recharge with low levels of tritium resulting in a concentration below 1 pCi/L, but still containing up to 20% recent recharge. Alternatively, these samples can contain recent recharge of agricultural irrigation supplied by groundwater wells producing pre-modern or fossil groundwater.

Table 4. Groundwater age classification

Age Tracer	Age Category			
	Fossil	Old/ Unknown	Mixed	Pre-1970, 1970-1980, 1980-1990, 1990-2000, 2000-2010, or Post-2010
Tritium (pCi/L)	< 1	< 1	≥ 1	≥ 1
Terrigenic helium (10^{-9} cm ³ STP/g)	≥ 5	< 5	≥ 5	< 5
³ H/ ³ He Age	ND	ND	Imprecise	Precise

2.4.5 Vertical Groundwater Age Gradients

To study the potential for young groundwater to transport nitrate to aquifer depths at which wells are screened, we examined the vertical groundwater age gradients. The vertical age gradient was calculated for each well as the distance between the midpoint of the well screen and the water table divided by the ³H/³He groundwater age.

$$g = (Z_{\text{MID}} - Z_{\text{WT}}) / \text{age}$$

With g the groundwater age gradient, Z_{MID} the midpoint of the well screen, Z_{WT} the depth of the water table, and age the ³H/³He groundwater age.

In an ideal unconfined aquifer, the vertical age gradient depends on the recharge rate and the thickness of the aquifer. In reality, many other factors influence the age of the water sampled at the well screen depth, such as spatial variations in recharge rate and regional groundwater flow patterns. Additionally, groundwater pumping can accelerate downward transport of young water. For example, regional lateral groundwater flow from mountain front recharge or river recharge can result in younger water at deeper depths than the local recharge rate can support. Groundwater pumping can induce a localized vertical flow drawing young water to greater depths. Regional discharge areas deliver older water closer to the water table. Evaluating the local groundwater flow system at each of the sampled well locations is beyond the scope of this study. The spatial analysis and interpolation of vertical age gradients performed here is intended to examine how groundwater flow paths and downward transport influence nitrate concentrations observed in wells in Central Coast groundwater basins.

We used the midpoint of the well screen to represent the depth of the sample. Groundwater mixing in long screened wells and by dispersion complicates a clear definition of the vertical age gradient. For wells with only information about the top of the screen or the depth of the well, the

midpoint was estimated based on linear regressions between the midpoint and the top or depth for wells which had all information available:

$$Z_{\text{MID}} = 1.1 * Z_{\text{TOP}} + 60 \text{ ft}$$

$$Z_{\text{MID}} = 0.78 * Z_{\text{DEPTH}}$$

The water table depth was calculated as the difference between a spatial interpolation of groundwater elevations in the GAMA dataset and the surface elevation of the 800 m resolution PRISM digital elevation model. Water tables above the land surface were set to zero. The gradient was calculated as vertical distance divided by groundwater age. This results in gradient close to zero in groundwater discharge areas, where old water is found near the groundwater table, rather than gradients approaching infinity. Apparent $^3\text{H}/^3\text{He}$ ages of zero years were mostly found close to the water table. These were omitted because they do not result in a reliable age gradient. Zero ages at depths greater than 100 ft below the water table were considered analytical errors and removed from this calculation. In addition to the $^3\text{H}/^3\text{He}$ groundwater ages, samples with evidence for fossil groundwater were included with an age gradient of zero.

2.4.6 Unsaturated Zone Travel Times

$^3\text{H}/^3\text{He}$ groundwater ages only capture the travel time below the water table and do not incorporate the unsaturated zone travel time. There are no practical age tracers for calculating the unsaturated zone travel time. Because the age gradient below the water table is influenced by regional hydrogeology and groundwater pumping, it is not a reliable metric for vertical flow through the unsaturated zone. Instead, we assume that vertical flow through the unsaturated zone is limited by a recharge rate of 1 foot per year. We acknowledge that infiltration rates across the study area are highly variable, but high rates of irrigation can induce high recharge rates and enhance vertical flow through the unsaturated zone. Assuming an effective porosity of 0.3 and a water saturation of 50%, the vertical age gradient in the unsaturated zone would be 7 ft per year. In most cases, unsaturated zone travel time did not add a significant amount of travel time from the land surface.

2.4.7 Metrics for Denitrification

Denitrification can reduce groundwater nitrate concentrations. To understand land use impacts on groundwater nitrate, it is important to quantify the effects of denitrification on groundwater nitrate concentrations. In this study, we used three metrics to study the effect of denitrification on groundwater nitrate concentrations: (1) the nitrogen and oxygen isotopes of nitrate, (2) the concentration of dissolved nitrogen gas in excess of atmospheric sources, and (3) trends in nitrate concentrations with respect to redox indicators.

2.4.7.1 Nitrate Isotopes

Denitrification of nitrate in soil and groundwater leads to isotopic fractionation, enriching the heavier isotopes of nitrogen (^{15}N) and oxygen (^{18}O) the residual nitrate, resulting in higher isotopic ratios in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ notation. The shift in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values follows a predictable trend which can often be distinguished from the signatures of the original nitrate source. The isotopic enrichment factors of denitrification are known with large uncertainty. If both the initial isotopic signatures and the enrichment factors are known precisely, the extent of denitrification can be quantified.

$$fd = \exp((\delta^{18}\text{O} - \delta^{18}\text{O}_{\text{initial}}) / \epsilon_{18\text{O}})$$

$$fd = \exp((\delta^{15}\text{N} - \delta^{15}\text{N}_{\text{initial}}) / \epsilon_{15\text{N}})$$

with fd the fraction of initial nitrogen denitrified, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ the measured isotope ratio of nitrate, $\delta^{15}\text{N}_{\text{initial}}$ and $\delta^{18}\text{O}_{\text{initial}}$ the initial isotope ratio of nitrate, and ϵ the enrichment factor.

Because neither initial isotopic ratios nor the enrichment factor is precisely known, they are estimated in this study by examining the progress of denitrification based upon the dissolved excess N_2 and nitrate concentrations.

2.4.7.2 Excess N_2

The end-product of denitrification of nitrate is nitrogen gas (N_2). Nitrogen gas produced below the water table dissolves in groundwater and cannot escape to the atmosphere. This results in dissolved nitrogen gas concentrations in excess of the initially dissolved concentration of nitrogen gas of atmospheric origin. Nitrogen gas dissolved in groundwater is not reactive and is transported conservatively by groundwater flow. As such it behaves similar to dissolved noble gases. There is a possibility that excess nitrogen gas causes bubble formation in groundwater but only if high concentrations of nitrate are denitrified at shallow depths below the water table.^{42, 43} Because this also results in partitioning of noble gases, this is easily detected.⁴⁴ If denitrification is partial (i.e. not all nitrate has been denitrified), both nitrate and excess nitrogen gas are present in groundwater. If the concentration of nitrate and excess nitrogen are both known, the initial nitrate concentration at the water table and the extent of denitrification can be calculated quantitatively as:

$$\text{NO}_3\text{-N}_{\text{in}} = \text{NO}_3\text{-N} + \text{N}_{2,\text{exc}}\text{-N}$$

$$fd_{\text{gw}} = \text{N}_{2,\text{exc}}\text{-N} / \text{NO}_3\text{-N}_{\text{in}}$$

with $\text{NO}_3\text{-N}_{\text{in}}$ the initial concentration of nitrate at the water table, $\text{NO}_3\text{-N}$ the observed concentration of nitrate, $\text{N}_{2,\text{exc}}\text{-N}$ the observed concentration of dissolved nitrogen gas in excess of the atmospheric component, and fd_{gw} is the fraction of initial nitrogen denitrified below the groundwater table. All nitrogen concentrations are expressed as milligrams of nitrogen per liter of groundwater, to accommodate the reaction stoichiometry and express results in the same unit as the nitrate MCL of 10 mg $\text{NO}_3\text{-N}$ per liter. Excess nitrogen has been used to reconstruct nitrogen inputs into heavily impacted aquifers in the U.S.,⁴⁵⁻⁴⁷ the Netherlands,³⁷ and Denmark.⁴³ This calculation assumes that intermediate nitrogen species (NO_2 , N_2O) are not present in significant concentrations.

We established a linear regression between the fraction of nitrate denitrified below the groundwater table (derived from excess nitrogen) and the isotopic fractionation trend caused by denitrification.

$$fd \sim \delta^{15}\text{N} + \delta^{18}\text{O} + c$$

Where fd is the fraction denitrified, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are the isotopic ratios of nitrogen and oxygen in nitrate, and c is a constant defining the source isotopic composition. We did not attempt to constrain the enrichment factors because excess nitrogen does not “record” the denitrification occurring in the unsaturated zone while nitrates isotopes do. The linear regression model between fraction denitrified and isotopic enrichment assumed all nitrate started with an isotopic signature similar to soil nitrogen. The regression excluded samples with isotopic values that are

indicative of fertilizer or septic/manure influences. The linear regression allowed us to study the extent of denitrification in relation to other geochemical or groundwater age metrics in all samples with either excess nitrogen or nitrate isotope measurements. The fraction denitrified was categorized as “no or limited denitrification” ($fd < 0.25$), “moderate denitrification” ($0.25 < fd < 0.75$), or “near-complete denitrification” ($fd > 0.75$).

2.4.7.3 Dissolved Oxygen as an Indicator for Denitrification

In addition to isotopic and dissolved gas evidence of denitrification, geochemical data were used to evaluate the oxidation and reduction reactions occurring in groundwater. The redox status is based on the scheme by McMahon⁴⁸ that uses the concentrations of dissolved oxygen, nitrogen, manganese, iron and sulfate to classify samples according to redox status. Data for all these parameters are only available for GAMA Priority Basin and Shallow Aquifer Assessment samples. This dataset was used to calculate the proportion of groundwater that has been subject to complete denitrification and is undergoing manganese or iron reduction. Other datasets (which did not have all necessary parameters available) were excluded because they resulted in a sampling bias. For example, combining a smaller dataset with oxygen data and a larger dataset with manganese and iron data resulted in an artificially high proportion of groundwater classified as anoxic (manganese or iron reducing) and a smaller proportion of oxic groundwater.

The extent of denitrification at the groundwater basin scale was also related to the dissolved oxygen concentrations measured in groundwater. The proportion of samples exceeding the MCL was calculated for anoxic ($DO < 1$ mg/L), intermediate ($1 < DO < 7$ mg/L), and oxic ($DO > 7$ mg/L) categories. Based on the proportion of MCL exceedances in anoxic and intermediate groundwater (which is lower than the proportion in oxic groundwater) the effectiveness of denitrification as a mechanism to protect groundwater quality was established.

3 Results

3.1 Nitrate Concentrations in Central Coast Groundwater Basins

Nitrate concentrations in Central Coast groundwater are high and spatially variable. The median nitrate concentration of all samples is 3.6 mg/L which is above the natural background nitrate concentrations of 3 mg/L defined by previous studies.⁴⁹⁻⁵² The 95th percentile of nitrate concentrations in Central Coast groundwater that recharged before 1950 was found to be 2.8 mg/L.⁵³ Nitrate concentrations above 3 mg/L are considered to have anthropogenic sources.^{54, 55} In all three study areas, more than 50% of samples have nitrate concentrations above 3 mg/L and are impacted by anthropogenic sources.

Nitrate concentrations are above the MCL in 29% of all samples (Table 5). Extremely high nitrate concentrations, above 100 mg/L, are found in 13 wells in Santa Maria Valley and 16 wells in Salinas Valley. Nitrate concentrations at these levels are typically associated with intensive agricultural practices^{56, 57} or point-source pollution.⁵⁸

Nitrogen concentrations in groundwater show a number of hot spots in the CCWB region (Table 5). Nitrate concentrations at the center of Santa Maria Valley are consistently above the MCL. Groundwater in the central part of the Salinas Valley contains some high and extremely high concentrations with greater variability over short distances.

Table 5. Nitrate concentrations in Central Coast groundwater basins

Study Area	Number of Samples	Above MCL		Anthropogenic Impact	
		NO ₃ -N > 10 mg/L	95%-CI ¹	NO ₃ -N > 3 mg/L	95%-CI
Santa Maria Valley	2249	35%	33%-37%	56%	54%-58%
Salinas Valley	3501	25%	24%-26%	51%	49%-53%
Gilroy-Hollister Valley	732	29%	26%-32%	64%	61%-67%
All samples	6482	29%	28%-30%	54%	53%-55%

¹CI: confidence interval

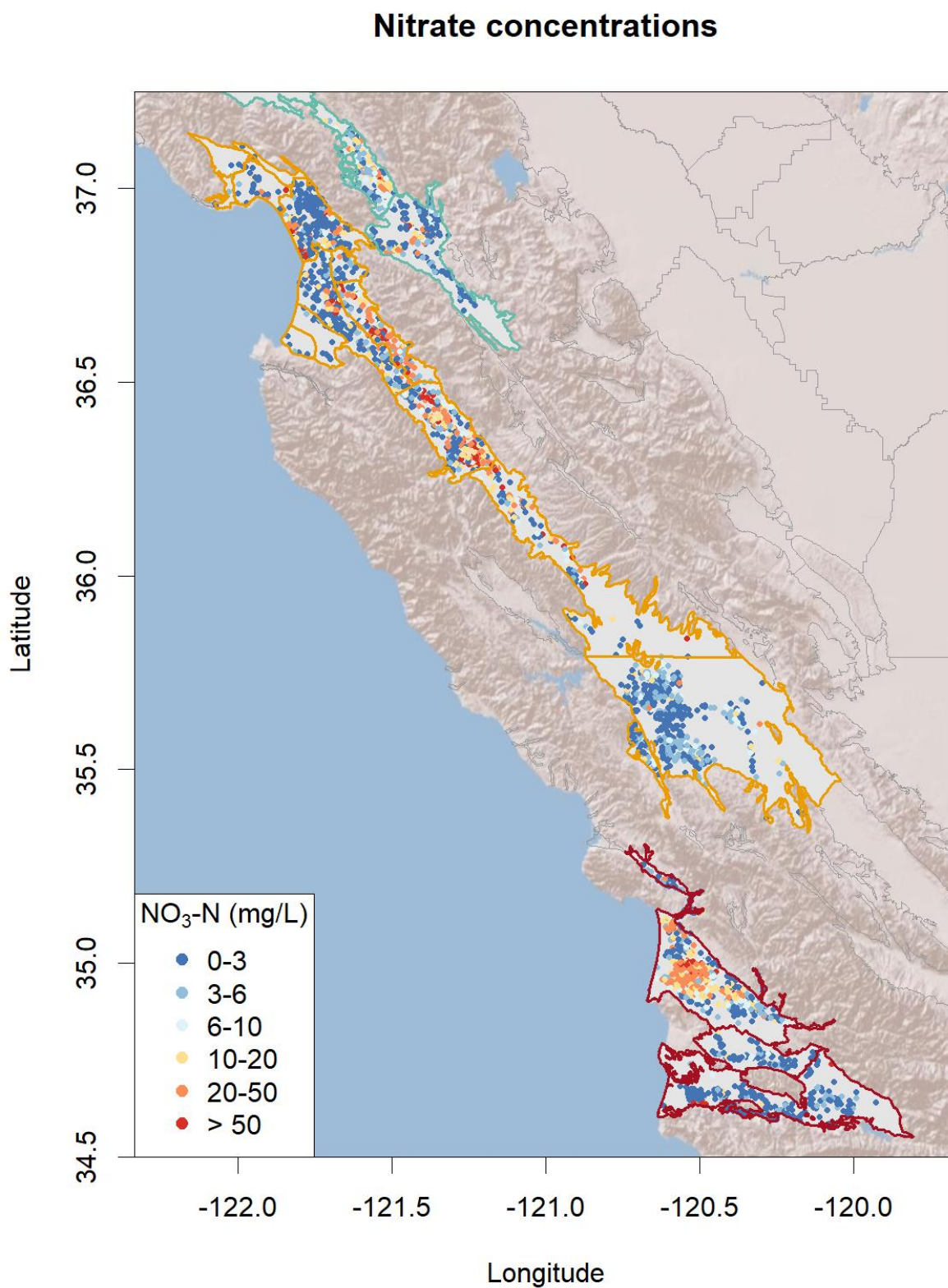


Figure 4: Nitrate concentrations (mg/L as N) in Central Coast groundwater.

3.2 Nitrate Sources

3.2.1 Isotopic Identification of Nitrate Sources

As a result of biological nitrogen cycling in soils, the isotopic signatures of nitrate, ammonia, and urea fertilizer are shifted and resemble the nitrogen isotopic signature typical of soil organic matter in most samples (Figure 5). Although the isotopic signature of groundwater nitrate cannot distinguish between natural soils and fertilized soils, the nitrate concentration indicates that agricultural nitrogen fertilizer is an important source to soil nitrogen.

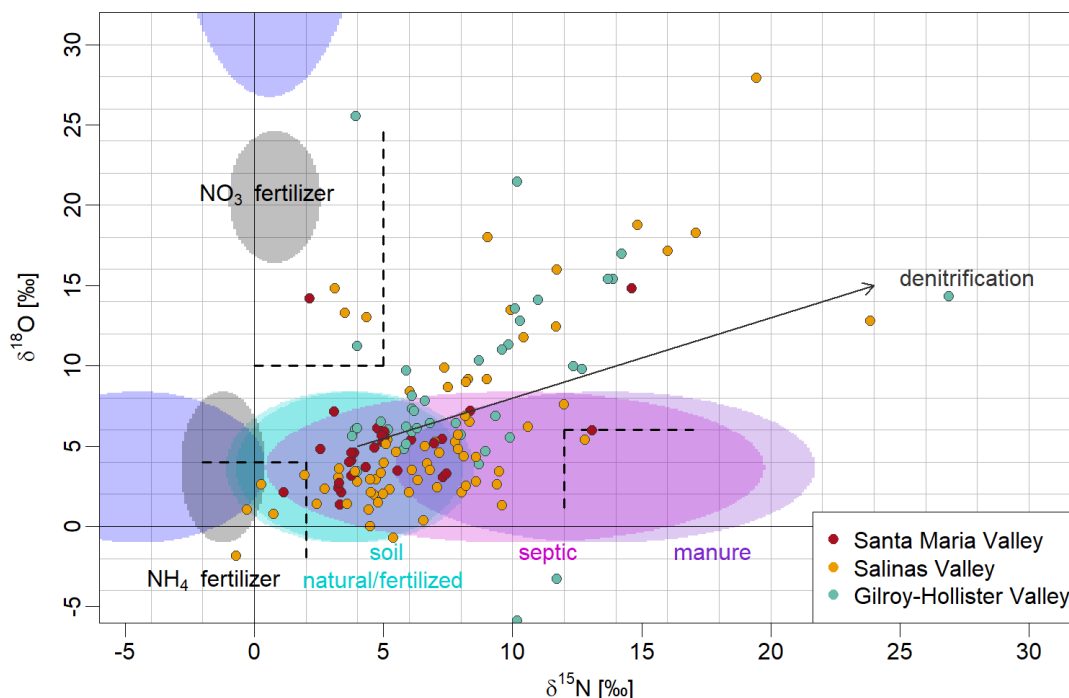


Figure 5: Measured nitrate isotopic signatures compared to potential sources

A few samples do not show evidence for significant alteration by biological cycling in soil. Nitrate isotopes identify a direct fertilizer source of groundwater nitrate in six samples with $\delta^{15}\text{N}$ below 5 ‰ and $\delta^{18}\text{O}$ above 10 ‰ (within the dashed partial box). The nitrate isotopic values of $\delta^{15}\text{N}$ below 2 ‰ and $\delta^{18}\text{O}$ below 4 ‰ in six samples suggest a direct contribution of ammonia or urea fertilizer to groundwater nitrate. Because the high $\delta^{15}\text{N}$ values indicative of septic or animal manure sources are also associated with denitrification, these sources are more difficult to identify. Two samples with $\delta^{15}\text{N}$ above 12 ‰ and $\delta^{18}\text{O}$ below 6 ‰ probably have a septic or manure source. The majority of samples resembles the isotopic signature of natural or fertilized soil because of biological nitrogen cycling, although the original source of nitrogen may have been artificial fertilizer. Isotopic fractionation by denitrification, causing a shift in nitrogen and oxygen isotopes, is discussed in Section 3.5.

3.2.2 Nitrate in Groundwater in Relation to Land Use and Nitrogen Application

The average amount of total nitrogen made available to crops on ranches reporting to the CCWB in 2018 (Table 6) is 541 pounds per acre per year (lbs/acre, including soil available nitrogen). For reference, an “operational benchmark” of 31 lbs of applied nitrogen per acre per year was suggested for the protection of groundwater quality by a UC Davis study.⁵⁹ Applied fertilizer is the main source of nitrogen made available to crops, contributing 60-67% of all nitrogen. Crop available soil nitrogen, released from the decaying organic matter from previous crops, contributes 13%-20%. Nitrate present in pumped groundwater used for irrigation is a significant source of nitrogen (22%). Aggregated over the three study areas, applied compost is not a significant source of nitrogen.

Table 6. Nitrogen available to crops

	Fertilizer [lbs/acre]	Soil Nitrogen [lbs/acre]	Irrigation [lbs/acre]	Compost [lbs/acre]	Total Nitrogen Application [lbs/acre]
Santa Maria Valley	362 (60%)	89 (15%)	151 (25%)	2 (0%)	605
Salinas Valley	348 (63%)	71 (13%)	121 (22%)	8 (1%)	548
Gilroy-Hollister Valley	249 (67%)	73 (20%)	47 (13%)	1 (0%)	370
All reports	340 (63%)	75 (14%)	120 (22%)	6 (1%)	541

Groundwater is the main source of water for irrigation in the Central Coast region. As a result, the calculated amount of nitrogen applied as nitrate dissolved in groundwater used for irrigation is directly determined by the amount of irrigation and the nitrate concentration in groundwater.

The relative contribution of sources of nitrogen was analyzed with respect to the total amount of applied nitrogen (Figure 6). Soil nitrogen contributes around 15% of all nitrogen available to plants, regardless of total nitrogen applied. Up to a total application of 600 lbs/acre, fertilizer nitrogen is the dominant source. Above 600 lbs/acre, fertilizer increases slightly to 600 lbs/acre but nitrate in groundwater used for irrigation becomes a substantial contribution to the total amount of nitrogen applied. Nitrate in pumped groundwater used for irrigation is a particularly significant source of nitrogen in operations where the total amount of applied nitrogen is above 1000 lbs/acre. The contribution of nitrate in pumped groundwater used for irrigation increases from 11% of less than 200 lbs applied N per acre to 40% of all nitrogen applied at rates over 1200 lbs/acre.

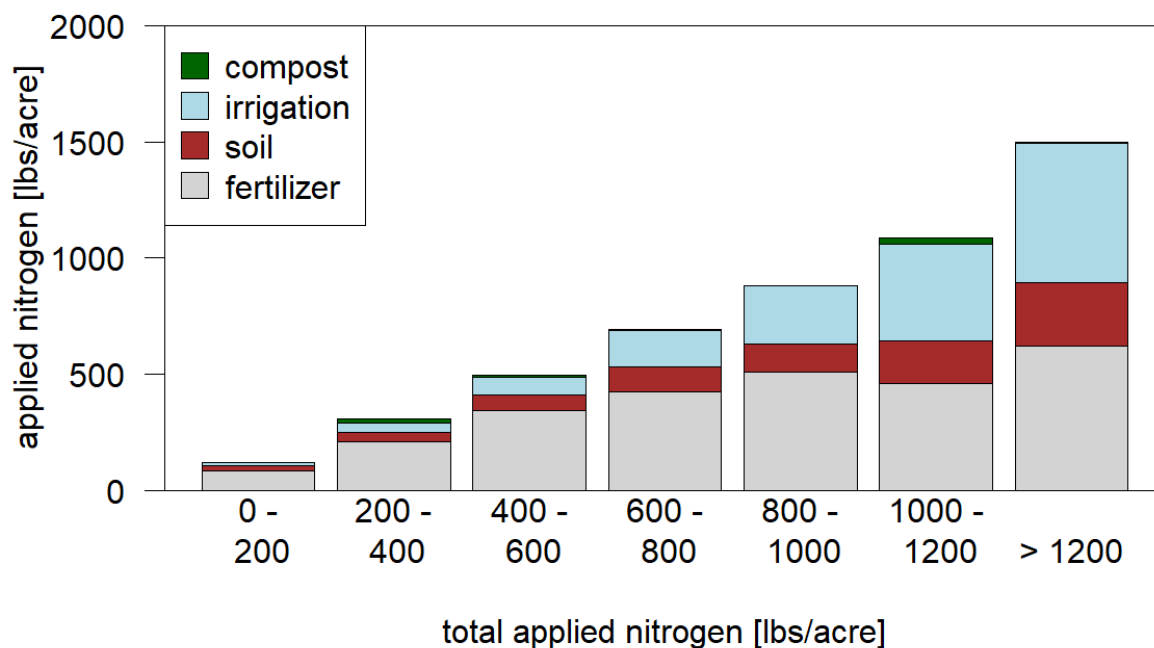


Figure 6: Nitrogen sources with respect to total N applied

A ternary plot shows how the contributions of different nitrogen sources vary with total nitrogen application rates (Figure 7). The size of symbols in the ternary reflect the total nitrogen application and the colors reflect the contribution of fertilizer (red), soil (green) and irrigation water (blue). Pure red, green or blue dots reflect a single dominant source, whereas a mixed color reflects more equal contributions of multiple sources. The sizes and colors of the ternary plot are used to visualize the spatial distribution of nitrogen applications from different sources. Total nitrogen applications vary considerably at short spatial distances.

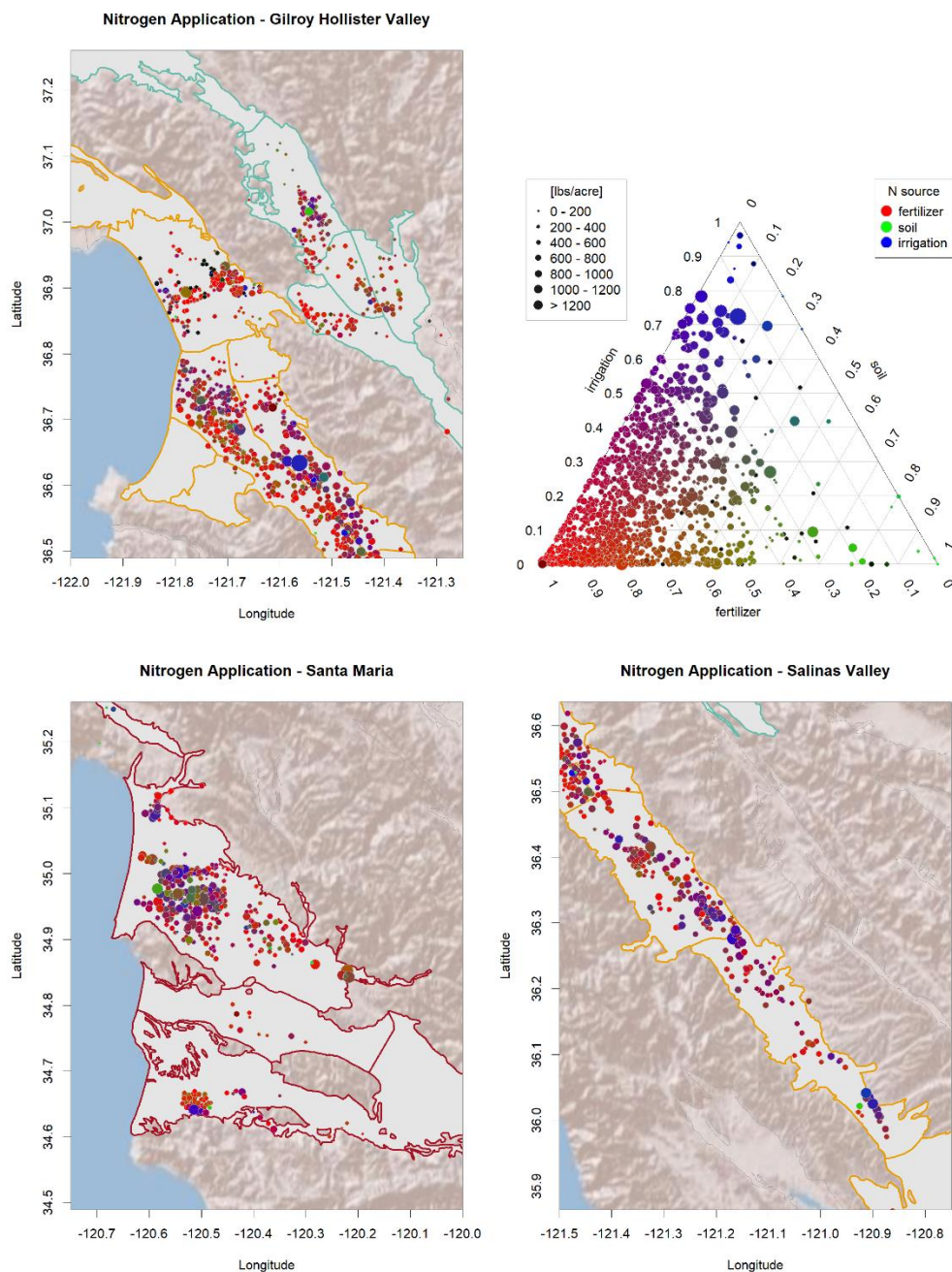


Figure 7: Ternary plot of total nitrogen application and contributions from different sources, mapped out on the three study areas within the CCWB region.

The highest average nitrogen applications are in Santa Maria Valley and the Salinas Valley (Figure 8). Hot spots of irrigation nitrogen are found on the western side of Santa Maria Valley and the southern part of the Salinas Valley (Figure 7). Spatial patterns of total applied nitrogen are similar to spatial patterns in nitrate concentrations, in part because of the application of irrigation water containing high nitrate concentrations.

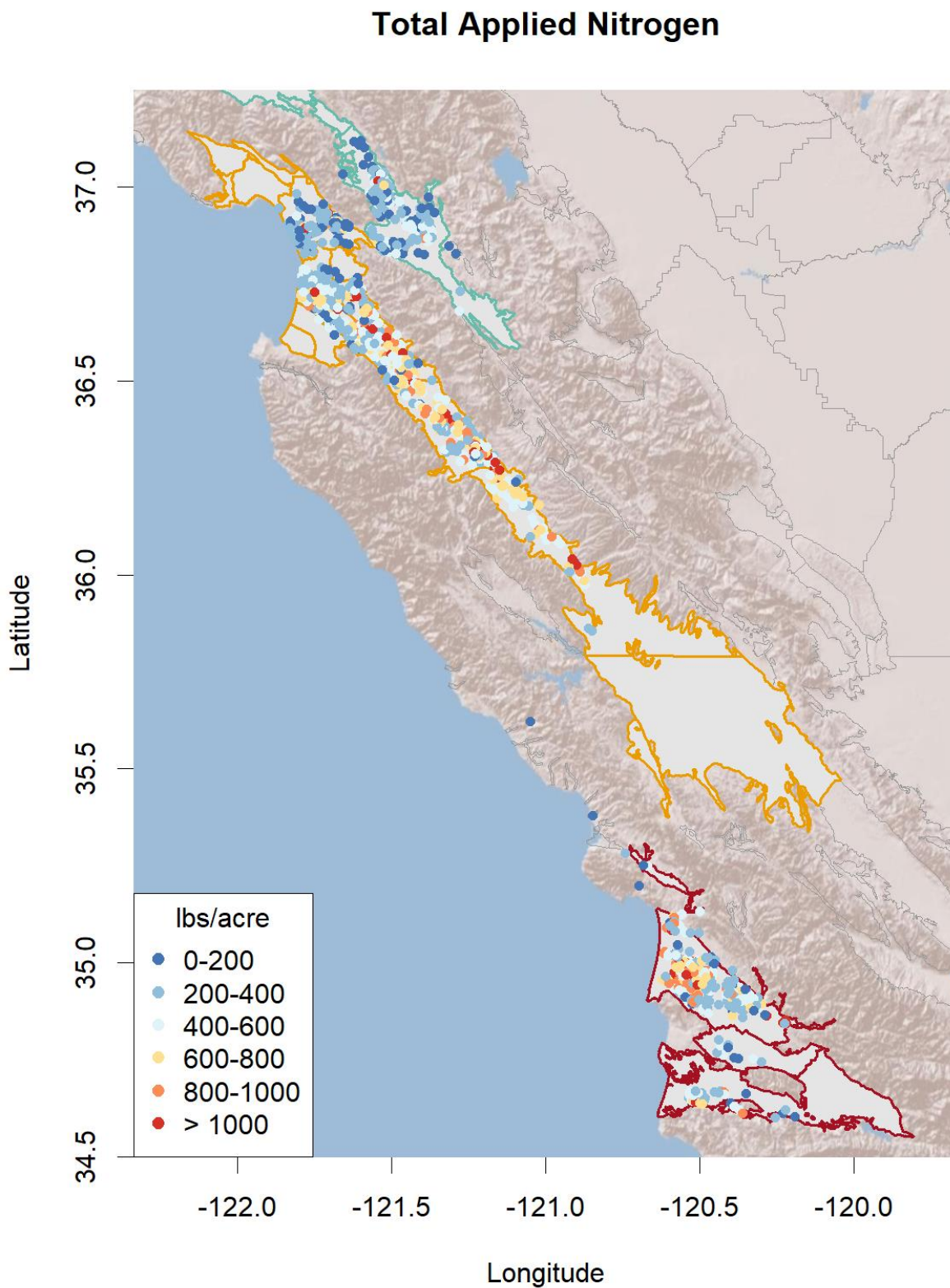


Figure 8: Total applied nitrogen reported by growers.

3.3 Groundwater Age and Nitrate Leaching History

3.3.1 Groundwater Age

A reliable $^3\text{H}/^3\text{He}$ groundwater age was calculated for 183 samples, nearly half of all samples with tritium and noble gas data. For these samples, the recharge year was calculated as the sample date minus the $^3\text{H}/^3\text{He}$ age (Figure 9). It should be noted that the recharge year reflects the moment that the water crossed the water table because $^3\text{H}/^3\text{He}$ age dating does not capture variability in vadose zone travel time or transport processes. To determine the relative importance of travel times in the unsaturated and saturated zones for the delay of nitrate reduction measures requires a suite of environmental age tracers ($^3\text{H}/^3\text{He}$, ^{85}Kr , ^{39}Ar , ^4He) which was beyond the scope of this study.⁶⁰ Most samples (114) have an estimated recharge year between 1990 and 2010. Few samples with a reliable $^3\text{H}/^3\text{He}$ age recharged before 1970 (6) or since 2010 (11).

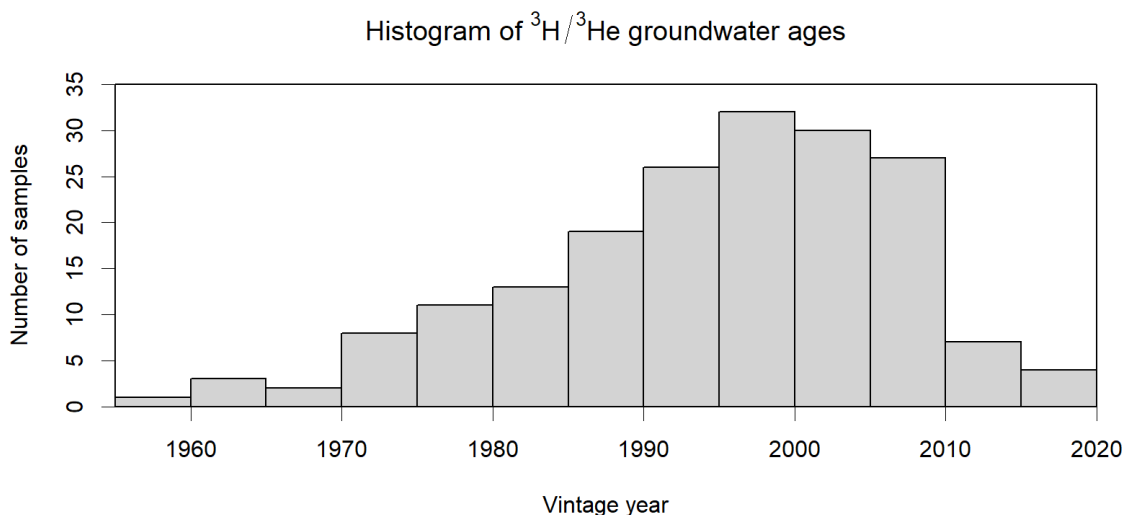


Figure 9: Histogram of $^3\text{H}/^3\text{He}$ recharge year.

The remainder of samples contained too little tritium or too much terrigenous helium (more than $5 \times 10^{-9} \text{ cm}^3\text{STP/g}$) to make a reliable age calculation. Instead, information about tritium and terrigenous helium concentrations was used to categorize samples as fossil, old/unknown or mixed. Fifty-six samples with a tritium concentration below 1 pCi/L and no terrigenous helium were classified as Old/Unknown. They are composed of pre-modern with no fossil component, or a mixture of ages that results in a low tritium and low terrigenous helium component. Seventy-five samples with a tritium concentration above 1 pCi/L and too much terrigenous helium to make a reliable calculation were classified as mixed. Seventy-six samples contained terrigenous helium and no tritium and were classified as “fossil” groundwater that has recharged over a thousand years ago.

Table 7. Groundwater age classification

Recharge Category	Fossil	Old/ Unknown	Mixed	Pre-1970	1970-1980	1980-1990	1990-2000	2000-2010	Post-2010
Samples	76	56	75	6	18	29	57	57	11
Percentage	20%	15%	19%	2%	5%	8%	15%	15%	3%

Groundwater ages generally increase with depth below the water table. ($R^2=0.68$, $p<0.001$) The steepest age gradients (resulting in young water at great depth) are close to 40 ft/yr in wells in Santa Maria Valley. The presence of young water at great depths indicates a focused source of recharge (e.g. direct river recharge) pushing young water downward or strong groundwater pumping in deep wells pulling young water downward. On the other hand, groundwater ages of up to several decades are observed in wells where the midpoint of the screen is near the mean annual depth to water. The calculated age gradient for these wells is zero. Samples with an apparent $^3\text{H}/^3\text{He}$ age of zero years are omitted from the spatial interpretation. Seventy-six wells with fossil water were added to the spatial analysis and assigned an age gradient of zero.

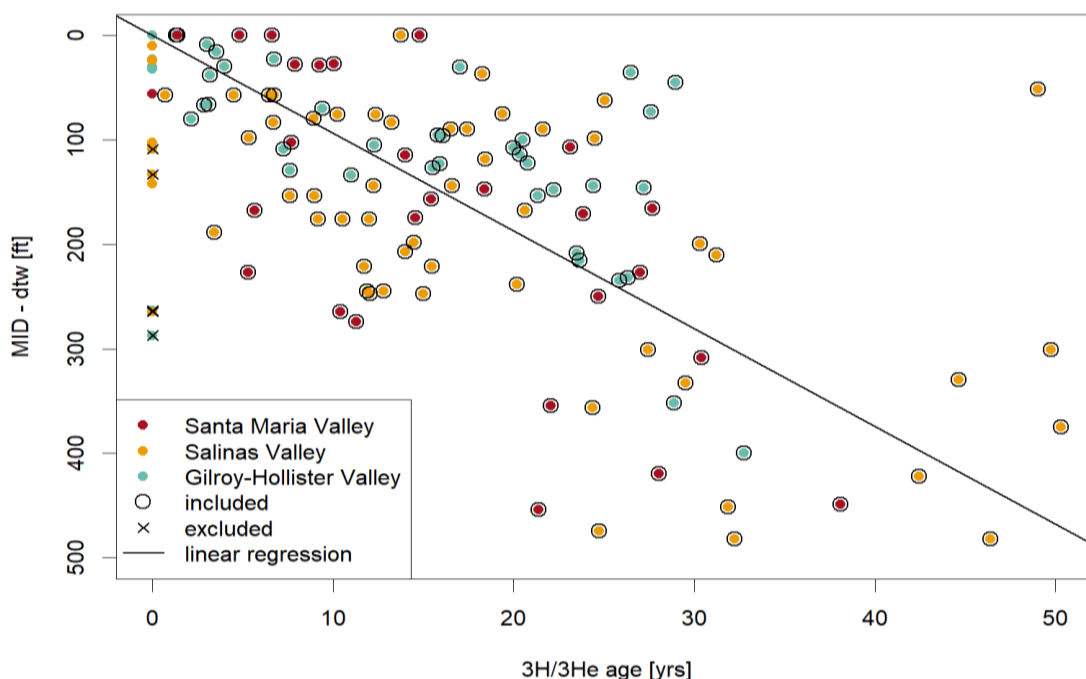


Figure 10: $^3\text{H}/^3\text{He}$ ages plotted at the vertical distance between the midpoint of the well screen (MID) and the water table (depth to water, dtw).

The vertical age gradients show a moderate spatial correlation up to 11 km. The short-range variability in age gradients is 50% of the total variability. The interpolated map (Figure 11) shows distinct patterns of high vertical age gradients in Santa Maria Valley, and moderate vertical age gradients in middle part of the Salinas Valley. High gradients are caused by deep

groundwater pumping, possibly in combination with river recharge and unconfined conditions. Low to zero vertical age gradients are found in the upper and lower parts of the Salinas Valley. These represent low groundwater recharge rates, confined conditions, and downgradient locations of a regional flow system.

To estimate the unsaturated zone travel time, we assumed a net recharge rate of 1 foot per year, a porosity of 0.3 and a 50% water saturation. This results in a vertical flow velocity of 7 feet per year. The median unsaturated zone travel times to the water table at the well locations is 11 years. For 75% of the wells, the calculated $^3\text{H}/^3\text{He}$ groundwater age (the travel time in the saturated zone) is larger than the unsaturated zone travel time. Therefore, we deem the $^3\text{H}/^3\text{He}$ groundwater ages to be a reliable indicator of the time of recharge and nitrogen leaching to the groundwater system.

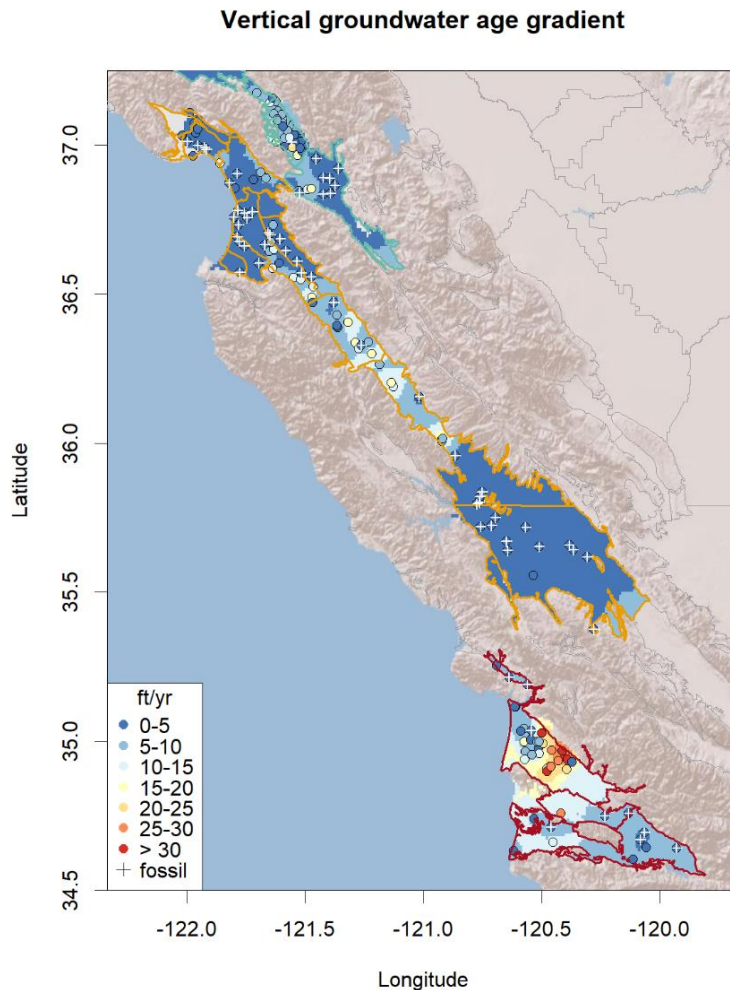


Figure 11: Map of interpolated vertical age gradients based on $^3\text{H}/^3\text{He}$ groundwater ages. + symbols indicate groundwater samples with fossil water.

3.3.2 Nitrate Leaching History

Nitrate concentrations above the MCL are found in all age categories (Figure 12), but they are least likely in fossil groundwater. The proportion of wells with a nitrate concentration above the

MCL in the fossil age category (8%) is significantly lower ($p < 0.01$) than the proportion in the remainder of the samples (25%). It is most likely that these 6 samples contain a mixture of ages, with a small modern component that contains too little tritium to be detected but enough nitrate to elevate the mixed concentration above the MCL. Low tritium concentrations in precipitation are likely the cause that modern groundwater—especially when recharged between 1980 and 2000—can go undetected by tritium analyses.

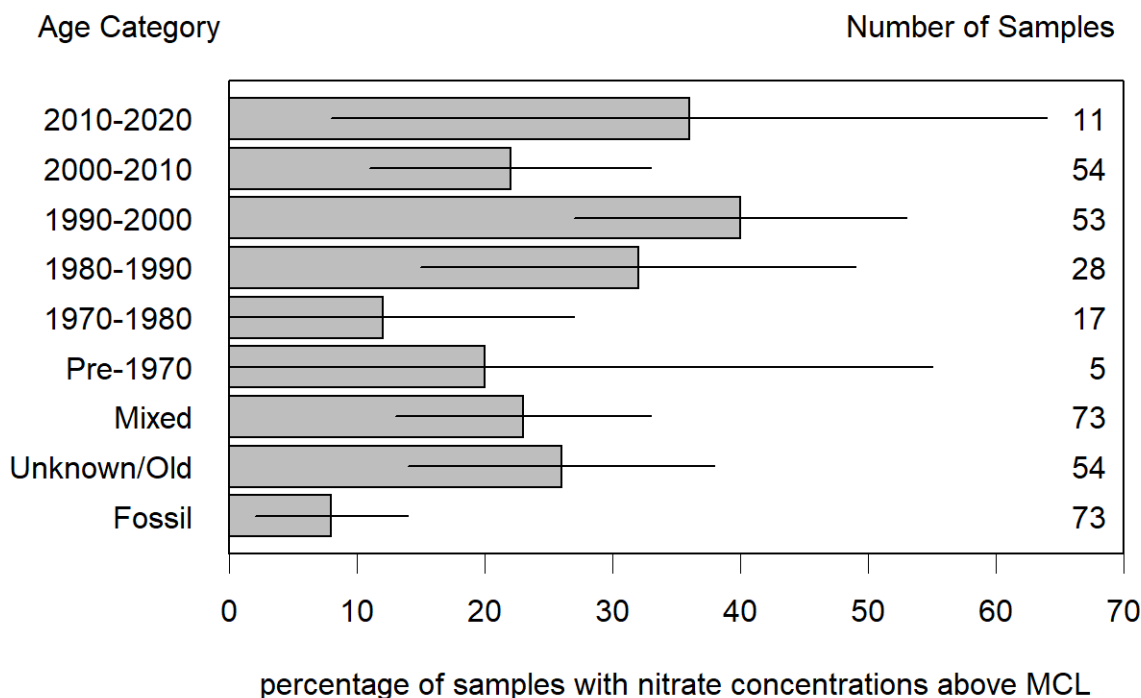


Figure 12: Proportion of samples with nitrate concentrations above the MCL within each age category

In all other age categories, the proportion of samples with a nitrate concentration above the MCL varies between 12% in the 1970-1980 age category and 40% in the 1990-2000 age category. The confidence intervals for all of these proportions largely overlap. Nitrate concentrations are above the MCL in 23% of the samples with mixed groundwater and 26% in the Unknown/Old category (groundwater with no evidence of modern (tritium) or fossil (terrigenic helium) components). These proportions are similar to the modern groundwater categories.

The lack of differentiation between the age categories suggests that high nitrate concentrations have leached to groundwater for decades. Long screens causing mixed groundwater ages also contribute to a limited sensitivity to trends in the proportion of nitrate concentrations above the MCL.

Few samples have recharged since 2010. The low number of wells with first-encounter groundwater makes it challenging to quickly evaluate the effect of a change in land use practices. We find no significant evidence that recent changes in land use practices have reduced the leaching of nitrate to groundwater.

3.4 Impact of River Water Recharge on Groundwater Nitrate Concentrations

We investigated whether the isotopic signature and noble gas composition of groundwater (indicative of the source and mechanism of recharge) explains the spatial variability of nitrate in groundwater in the Santa Maria Valley. The $\delta^{18}\text{O}\text{-H}_2\text{O}$ value of precipitation correlates strongly with precipitation, with lower values at higher elevations. The mean elevation of the catchment area of the Cuyama and Sisquoc rivers is 915 m and 980 m, respectively. Based on a $\delta^{18}\text{O}\text{-H}_2\text{O}$ analysis of water in the Santa Barbara Canyon (-8.31 ‰ with a catchment elevation of 1328 m) and analyses from Oso Flaco Creek at sea level (-5.91 ‰), the $\delta^{18}\text{O}\text{-H}_2\text{O}$ value of Cuyama and Sisquoc Rivers is estimated to be -7.6 ‰.

River water is not used for irrigation directly in Santa Maria Valley. Instead, Twitchell Reservoir on the Cuyama River impounds winter floodwaters for later release down the river channel at a predetermined rate for maximum percolation into the groundwater reservoir. Individual landholders pump water from this reservoir.^{61, 62}

$\delta^{18}\text{O}\text{-H}_2\text{O}$ values in groundwater vary from below -6.6 ‰, indicating a component of water from Santa Maria River, to above -6 ‰, indicating local precipitation recharge. $\delta^{18}\text{O}\text{-H}_2\text{O}$ values in between these endmembers indicate a mixture of recharge sources. Low $\delta^{18}\text{O}\text{-H}_2\text{O}$ values in groundwater at the eastern side of Santa Maria Valley indicate river water is a source of groundwater recharge. The “plume” of river water recharge extends southwest, while Santa Maria River runs further along the northern edge of the valley before turning southwest. Strong vertical age gradients are found in an area where water isotopic signatures indicate local precipitation recharge, rather than river water recharge. This suggests that deep groundwater pumping—and not river water recharge—is causing strong vertical age gradients.

Low noble gas temperatures are further evidence of river water recharge during the colder winter season, whereas higher noble gas recharge temperatures are found in areas with local precipitation recharge or infiltration of hillslope runoff.

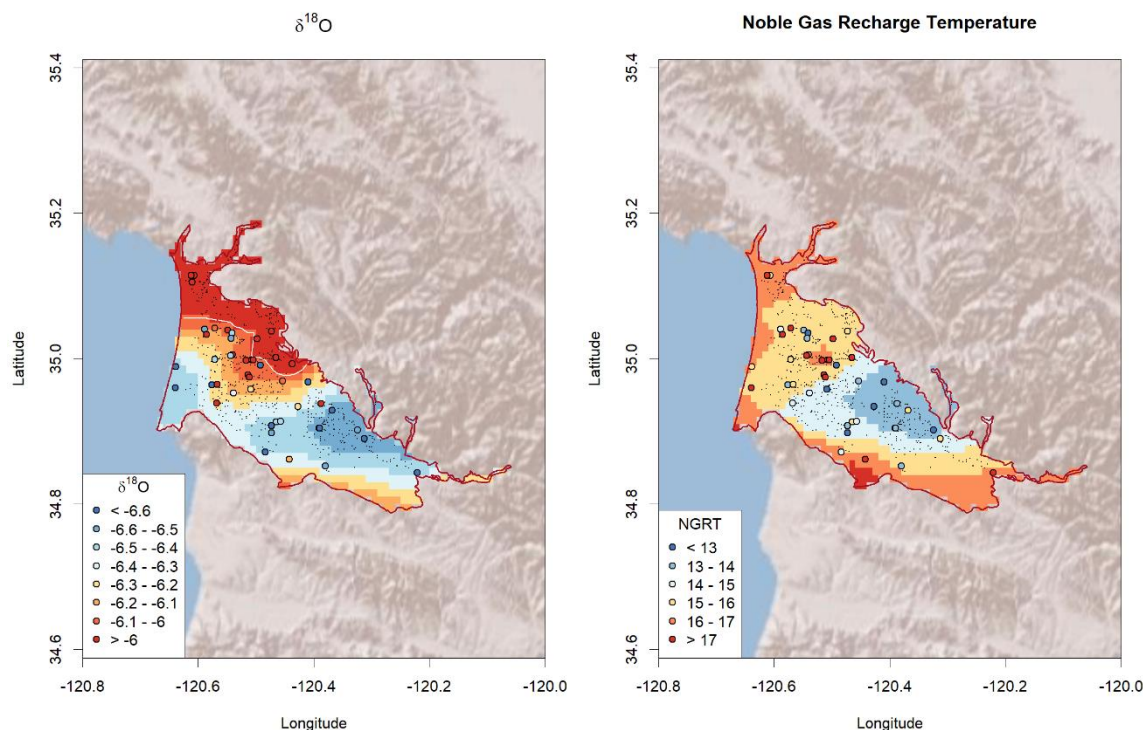


Figure 13: Interpolated maps of $\delta^{18}\text{O}$ and noble gas recharge temperature show the extent of river water recharge in the eastern portion of Santa Maria Valley.

While 50% of groundwater samples from the Santa Maria groundwater basin have a nitrate concentration above the MCL, groundwater with evidence of river water recharge contains lower nitrate concentrations. Boxplots of nitrate with respect to mapped $\delta^{18}\text{O}$ and noble gas recharge temperature show how the recharge mechanism influences nitrate concentrations. In areas where the mapped $\delta^{18}\text{O}$ -H₂O values are below -6.4 ‰, indicative of Santa Maria River water, 35% of wells have a nitrate concentration above the MCL. This proportion increases sharply to 70% for wells with a $\delta^{18}\text{O}$ -H₂O of between -6.3 ‰ and -6 ‰, indicative of local precipitation recharge. In the northwestern portion of Santa Maria Valley, nitrate concentrations above the MCL are found in 35% of wells, where groundwater $\delta^{18}\text{O}$ -H₂O values are above -6 ‰.

In the Santa Maria groundwater basin, the proportion of wells with nitrate concentrations above the MCL is approximately 50% regardless of noble gas recharge temperature. However, in parts of the Santa Maria groundwater basin with mapped recharge temperatures below 14 °C, the mean nitrate concentrations (12.8 mg/L) and the proportion of wells with a nitrate concentration above 20 mg/L (19%) are significantly lower than in the remainder of the valley (18.2 mg/L and 31%).

Analysis of nitrate concentrations with respect to $\delta^{18}\text{O}$ -H₂O and noble gas recharge temperatures in Santa Maria Valley shows that nitrate concentrations are lower in groundwater with a river water recharge source than in groundwater recharged by local precipitation or local groundwater-irrigation return flow. While river water recharge results in lower nitrate concentrations, a significant proportion of wells in areas of river water recharge still contain nitrate in excess of the MCL. The level of nitrate concentrations and the proportion of wells with nitrate above the

MCL in sample with a river water signature suggests that these wells sample a mixture of river water recharge and agricultural recharge or that this signature represents irrigation return flows from pumped groundwater that originally recharged as river water. Direct recharge of Santa Maria River water would result in nitrate concentrations well below the MCL.

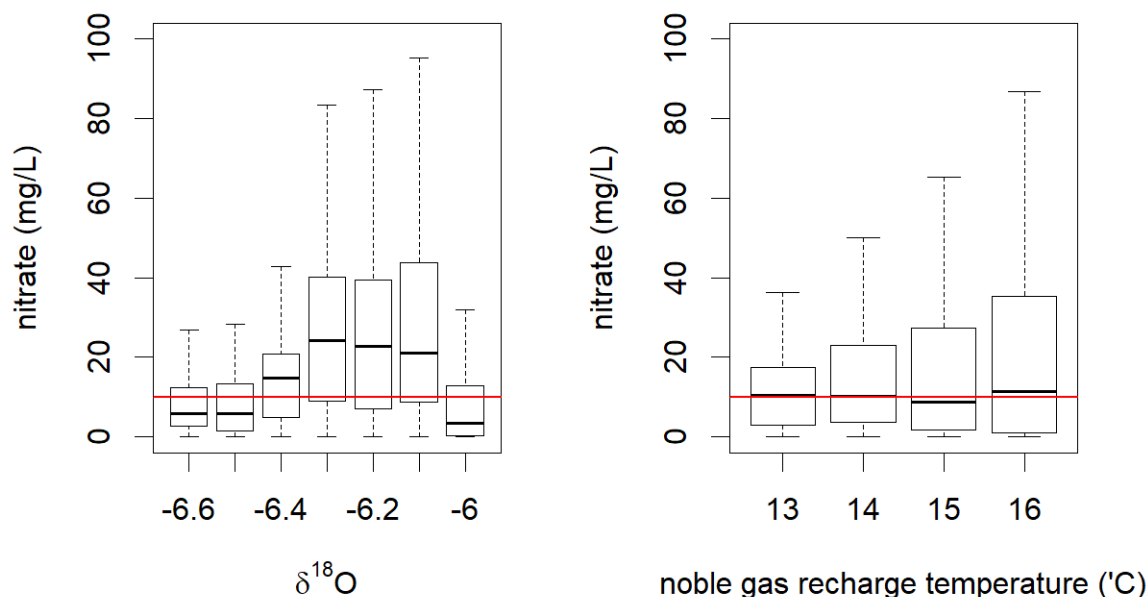


Figure 14: Nitrate concentrations with respect to $\delta^{18}\text{O}\text{-H}_2\text{O}$ and noble gas recharge temperatures in Santa Maria Valley.

Consistent patterns between $\delta^{18}\text{O}\text{-H}_2\text{O}$ and nitrate were not observed in either Salinas Valley or Gilroy-Hollister Valley. While we expect that the same mechanisms influence nitrate concentrations in these basins, the resolution of our data set may not be sufficient to capture the complex groundwater – surface water interactions of the Salinas River and different sources of recharge in Gilroy-Hollister Valley.

3.5 Denitrification

Denitrification has the potential of reducing nitrate concentrations and limiting the proportion of groundwater with a nitrate concentration above the MCL. We used three metrics of denitrification based on dissolved gas analyses, nitrate isotopes, and groundwater chemistry to answer how prevalent denitrification is in the region and how effective denitrification is in reducing nitrate concentrations below the MCL.

3.5.1 Fraction Denitrified Nitrate

The fraction denitrified nitrate (fd) was calculated from measurements of excess dissolved nitrogen gas in 83 samples. Values for fd range from 0% (no evidence for denitrification) to

100% (complete denitrification). Nearly 40% of samples show little evidence of denitrification ($fd < 25\%$) and nearly 25% of samples show a high fraction of denitrification ($fd > 75\%$).

The estimated fraction denitrified calculated directly from the isotopic fractionation of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate is very sensitive to the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the initial nitrate. Instead, we found that fd correlates well with both $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ of nitrate (Figure 15). A high fraction denitrified (fd calculated from excess dissolved $\text{N}_2 > 75\%$) is typically associated with $\delta^{15}\text{N}\text{-NO}_3$ values above 16 ‰ or $\delta^{18}\text{O}\text{-NO}_3$ values above 20‰. A low fraction denitrified is typically associated with $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ values below 6‰. A few samples have a large excess dissolved N_2 component (and high fd) but isotopic values similar to lower fd values. This combination is likely caused by in-well mixing of anoxic groundwater (with high excess N_2 and no nitrate) and oxic groundwater (with low excess N_2 and high nitrate). The isotopic composition in such a mixture reflects the nitrate in the oxic component.

A multiple linear regression model to calculate the fraction denitrified was constructed based on 52 samples with both excess nitrogen and nitrate isotopes (out of 126 with nitrate isotope data):

$$fd = 0.032 \delta^{15}\text{N} + 0.014 \delta^{18}\text{O} - 0.046$$

This regression is represented by dashed lines in Figure 15. Thirteen samples with isotopic signatures resembling fertilizer or septic/manure sources were excluded from the regression (indicated on with \times symbols). The linear model has a residual standard error of 0.18 on 49 degrees of freedom and an R-squared of 0.63. The fraction denitrified was calculated in 80 samples based on this regression, in addition to 83 samples for which excess dissolved nitrogen data were available to calculate fd .

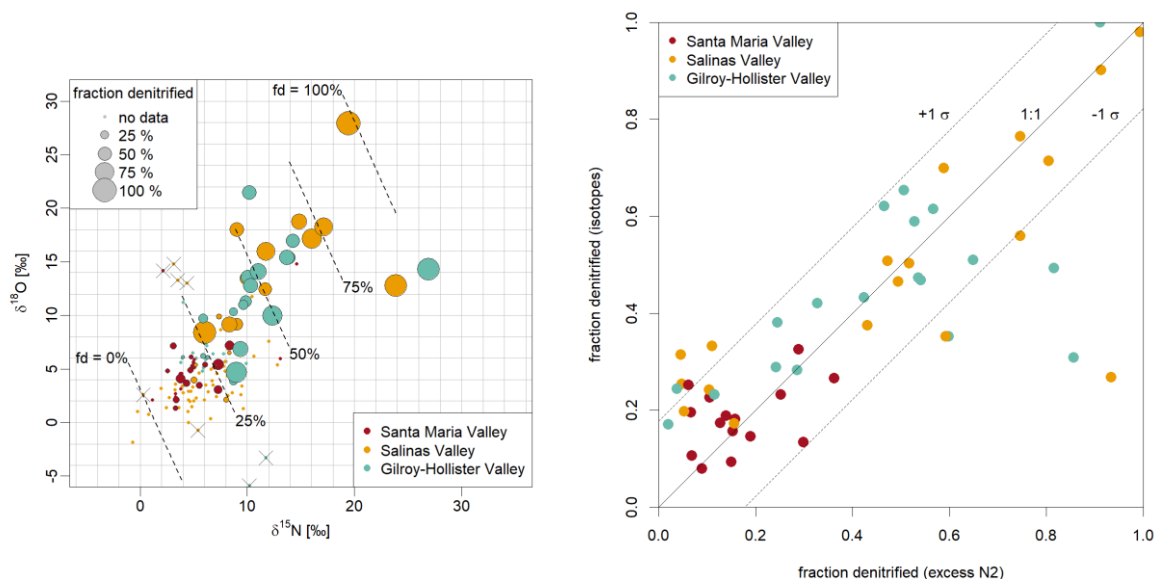


Figure 15: Relationship between nitrate isotopes and fraction denitrified nitrate based on excess dissolved N_2 .

Overall, we find little evidence for denitrification ($fd < 25\%$) in 48% of all samples (Table 8). Denitrification is less common in Santa Maria Valley, where 79% of samples show little evidence of denitrification. A high fraction denitrified was not detected in any of the 29 Santa

Maria samples. Denitrification is more likely to transform most of the nitrate in Gilroy-Hollister Valley (fd > 75% in 18% of 55 samples) than in Salinas Valley (9% of 77 samples).

Table 8. Fraction denitrified based on isotopic or dissolved gas evidence.

Area	Samples	Fraction Denitrified (fd)			
		0-25%	25-50%	50-75%	75-100%
Santa Maria Valley	29	79%	14%	7%	0%
Salinas Valley	77	48%	35%	8%	9%
Gilroy-Hollister Valley	55	38%	38%	13%	18%
All samples	161	48%	32%	9%	11%

In samples with limited evidence for denitrification (fraction denitrified less than 25% based on isotopic or excess nitrogen evidence), the proportion of samples with nitrate concentrations above the MCL is 55% (Table 9). The proportion of samples with nitrate concentrations above the MCL decreases with increasing fraction denitrified. Nitrate concentrations were below the MCL in all samples with a high fraction denitrified (fd > 75%). Because this study and prior studies including nitrate isotopes or excess nitrogen were focused on areas and wells with high known nitrate concentrations, the proportion of samples with a nitrate concentration above the MCL within this subset of the data is higher (37%) than for all available data (29%). To further study the reasons for variable occurrence and fraction denitrified, we correlate the fraction denitrified to dissolved oxygen concentrations.

Table 9. Proportion of samples with a nitrate concentration above the MCL for different fractions denitrified.

	Fraction Denitrified (fd)				All samples
	0-25%	25-50%	50-75%	75-100%	
Number of samples	77	52	15	17	161
Proportion with nitrate concentration above MCL	55%	33%	7%	0%	37%
Confidence Interval	44%-66%	20%-46%	0%-20%	-	30%-44%

3.5.2 Dissolved Oxygen

A larger set of dissolved oxygen concentrations provide additional information about the effectiveness of denitrification to reduce nitrate concentrations below the MCL and the prevalence of denitrification in Central Coast groundwater. Our detailed understanding of denitrification was based on isotopic and dissolved gas measurements (161 samples) and extended to a larger dataset (1983 samples) based on dissolved oxygen concentrations. We find that the fraction denitrified nitrate fd is correlated with the measured dissolved oxygen

concentration (Figure 16). In samples with a dissolved oxygen concentration below 1 mg/L, the fraction denitrified nitrate is close to 1. The fraction denitrified drops sharply with oxygen concentrations above 1 mg/L and is variable up to 7 mg/L oxygen. Because denitrification is thermodynamically less favorable than oxygen consumption, it is often assumed that it does not occur in groundwater with dissolved oxygen present. The gradual transition of the fraction denitrified between 1 and 7 mg/L dissolved oxygen can be attributed to micro-scale sites of anoxia in groundwater where denitrification can occur while the majority of groundwater is oxic and to the mixing of oxic and anoxic flow paths at long screened wells.

We find that samples with a dissolved oxygen concentration above 7 mg/L (representing 25% of all wells with oxygen concentrations) show little isotopic evidence for denitrification (the median fraction denitrified is below 0.2). We conclude that denitrification does not affect nitrate concentrations in groundwater with a dissolved oxygen concentration above 7 mg/L. We therefore use a subset of samples with more than 7 mg/L dissolved oxygen to represent the concentrations of nitrate that leach to groundwater.

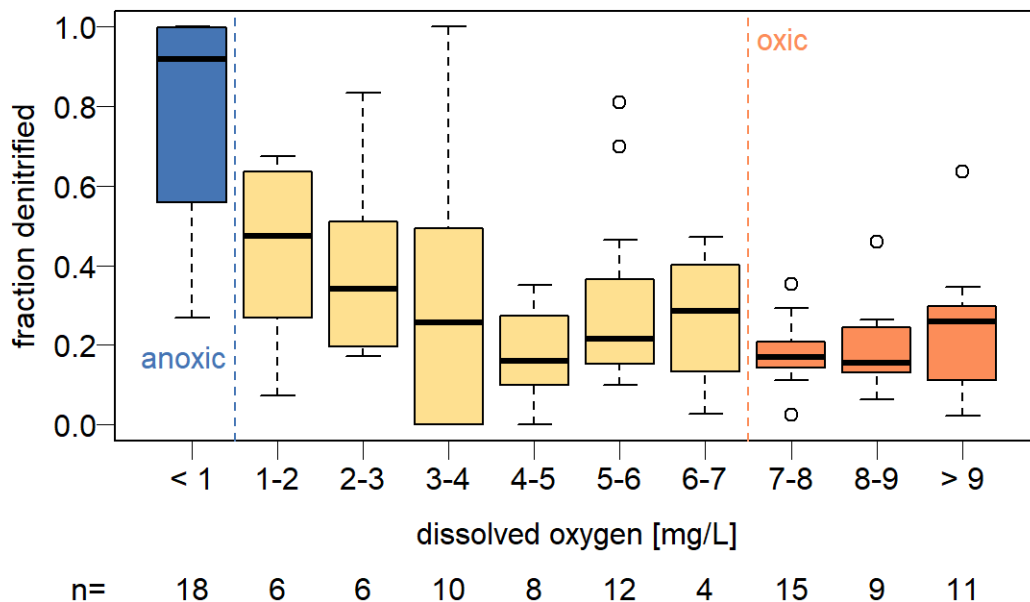


Figure 16: Relationship between the fraction denitrified nitrate and the dissolved oxygen concentration.

The larger set of samples with dissolved oxygen concentrations (1983 samples) provides a better estimate of the prevalence of denitrification in Central Coast groundwater. We find that dissolved oxygen concentrations are below 1 mg/L in 24% of all samples, and above 7 mg/L in 24% of all samples (Table 10). These proportions are very similar in all three study areas.

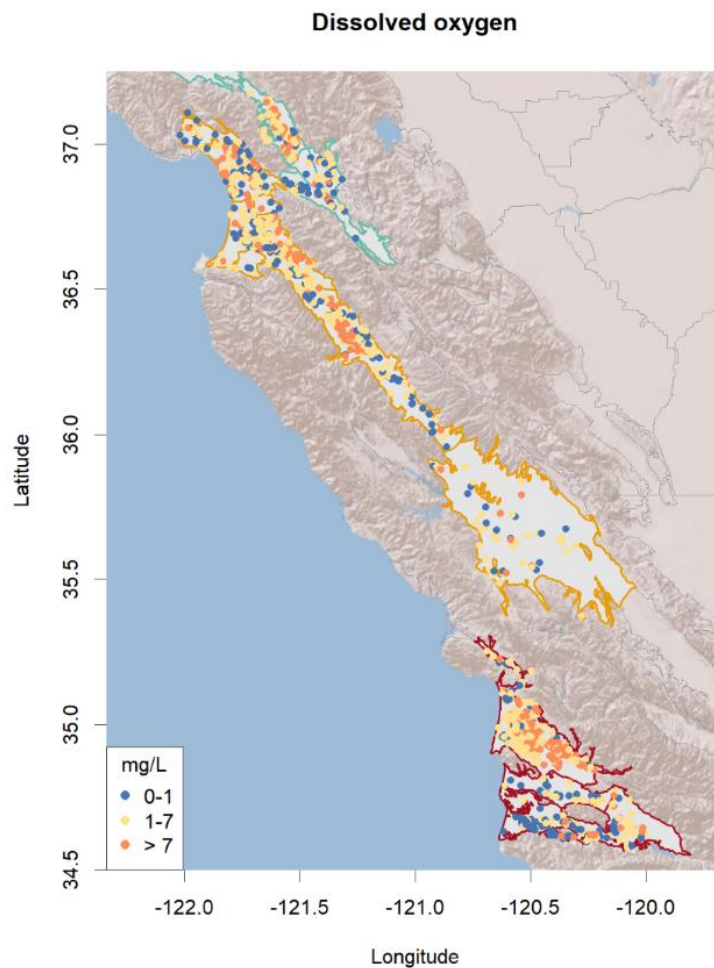


Figure 17: Map of dissolved oxygen.

Table 10. Proportion of samples with oxygen concentrations below 1 mg/L, between 1 and 7 mg/L and above 7 mg/L.

Area	Samples	Dissolved oxygen concentration		
		< 1 mg/L	1-7 mg/L	> 7 mg/L
Santa Maria Valley	1027	24%	50%	26%
Salinas Valley	710	25%	54%	21%
Gilroy-Hollister Valley	246	23%	55%	22%
All samples	1983	24%	52%	24%

To estimate the effect of denitrification on nitrate concentrations, we study the proportion of wells with nitrate above the MCL in each of the dissolved oxygen categories. In wells with more than 7 mg/L dissolved oxygen, nitrate concentrations exceed the MCL in 52% of the samples. In samples with a dissolved oxygen concentration below 1 mg/L, 18% exceed the MCL. Therefore,

a dissolved oxygen concentration of less than 1 mg/L does not guarantee complete removal of all nitrate by denitrification.

Spatial patterns of dissolved oxygen show distinct areas with high concentrations in the northeastern side of Santa Maria Valley, the northern half of Salinas Valley, and the northern side of Gilroy-Hollister Valley (Figure 17). These areas overlap with areas of high vertical age gradients. Efficient recharge and deep groundwater introduce more oxygen to these parts of the groundwater system.

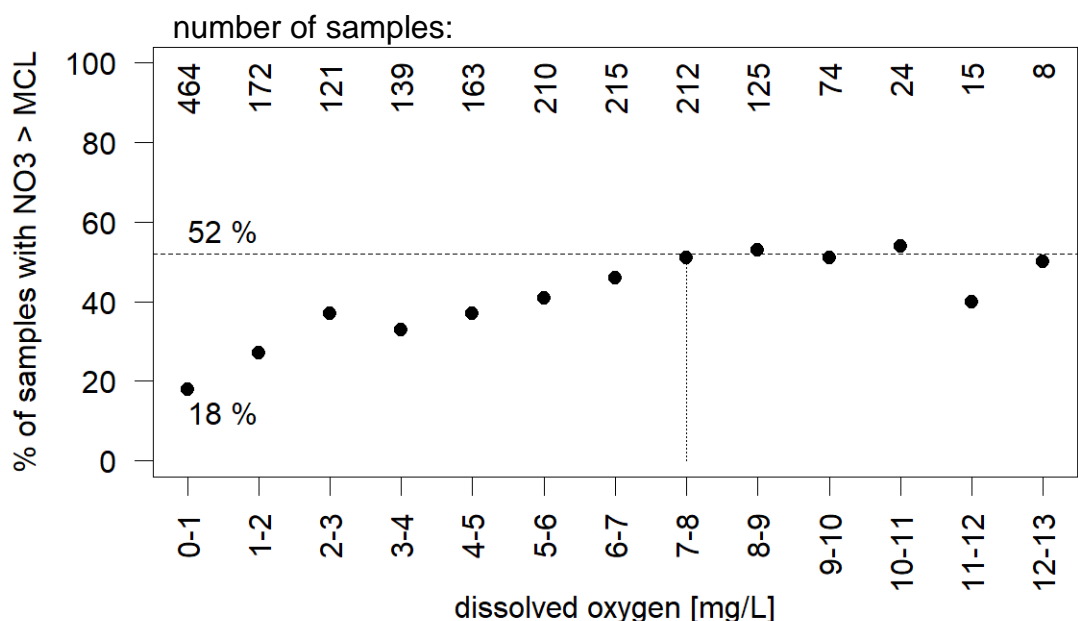


Figure 18: Relationship between the proportion of samples with nitrate concentrations above the MCL and the dissolved oxygen concentration.

3.5.3 Denitrification as a Mechanism to Reduce Nitrate Concentrations Below the MCL

Nitrate concentrations are above the MCL in 52% of samples with high oxygen concentrations (Figure 18). We assume that proportion reflects the nitrate concentrations at the time of groundwater recharge, because the effects of denitrification are not observed in groundwater with oxygen concentrations above 7 mg/L. We therefore estimate that, for the remaining 48% of samples, nitrate concentrations were below the MCL at the time groundwater recharge. In the subset of samples with DO data, nitrate concentrations are below the MCL in 64% of samples. If nitrate was below the MCL at the time of recharge in 48% of cases, the difference between these proportions (64% - 48% = 16%) can be attributed to the effect of denitrification (Table 11). In these wells, denitrification reduced the concentration from above the MCL when water was leaching from the root zone to below the MCL by the time the groundwater was sampled. While denitrification can protect groundwater from nitrate concentrations above the MCL, we find that applies to a small subset of wells (16%) within the Central Coast region. While aquifer locations

and depths where dissolved oxygen concentrations are <1 mg/L have a high assimilative capacity for nitrate, these account for only 24% of all samples.

Table 11. Proportion of wells with nitrate concentrations above the MCL in wells with DO data.

Area		All samples with DO data	Samples with DO > 7 mg/L	Nitrate concentration below MCL because of denitrification
All areas	Number of samples	1950	466	
	above MCL	36%	52%	
	below MCL	64%	48%	16%
Santa Maria Valley	Number of samples	1006	266	
	above MCL	40%	56%	
	below MCL	60%	44%	16%
Salinas Valley	Number of samples	700	145	
	above MCL	35%	53%	
	below MCL	65%	47%	18%
Gilroy-Hollister Valley	Number of samples	244	55	
	above MCL	26%	31%	
	below MCL	74%	69%	6%

The proportion of wells with a nitrate concentration below the MCL because of denitrification is similar in Santa Maria Valley (16%) and Salinas Valley (18%). In Gilroy-Hollister Valley, the proportion of wells with nitrate above the MCL in oxic groundwater starts off lower (31% of 55 samples) than in the other two areas. Denitrification reduces this proportion to 26%, and in this area only 6% of wells have a nitrate concentration below the MCL because of denitrification.

Without denitrification occurring in soils and groundwater, nitrate concentrations would exceed the MCL in more wells. However, denitrification is not effective in protecting groundwater against nitrate contamination because it is not sufficiently widespread and advanced to reduce nitrate concentrations below the MCL in all groundwater.

3.5.4 Denitrification Trends with Groundwater Age or Depth

The fraction denitrified or dissolved oxygen concentrations do not show a trend with calculated groundwater ages or the depth of the well screen. The proportion of samples with little evidence of denitrification ($fd < 0.25$) is lower for fossil (29%) or mixed age groundwater (42%) than for all data on average (59%). The proportion of samples with high oxygen concentrations ($DO > 7$ mg/L) decreases from 18-27% in modern groundwater to 9-12% in samples with mixed or

unknown groundwater age, to 1% in fossil groundwater. Lower proportions of fd and high DO are observed in younger groundwater, but confidence intervals for these proportions largely overlap. Denitrification and oxygen depletion appear to progress over long times scales. Our data does not show denitrification progressing on decadal time scales.

The proportion of wells with nitrate concentrations above the MCL decreases with depth to zero for wells with the top of the screen below 600 ft. However, the redox parameters (fd, DO) show no trend with depth. For example, neither the proportion of wells with a dissolved oxygen concentration above 7 mg/L or below 1 mg/L varies substantially with depth. The absence of clear patterns with age and depth are likely due to long well screens and the layered aquifer systems with confining units.

4 Discussion

4.1 Characteristics of Wells with Nitrate Above the MCL

To study how wells with nitrate concentrations above the MCL are different from wells with nitrate concentrations below the MCL in terms of nitrogen application, denitrification, recharge, and groundwater age, we performed a series of t-tests (Table 12). The mean of the following characteristics was compared for the “above” and “below” the MCL subsets of samples: nitrogen application rates, denitrification related parameters, groundwater age metrics, and recharge metrics. We find statistically significant differences in mean values for these characteristics at the 95% confidence level ($p < 0.05$).

4.1.1 Nitrogen application

It should be noted that the nitrogen application rates are reported for 2018, whereas groundwater ages show that the high nitrate concentrations in most groundwater samples have leached into the groundwater several decades ago. We find that higher application rates of fertilizer N (34 lbs/acre), soil N (17 lbs/acre), and total N (194 lbs/acre) in the subset of wells with a nitrate concentration above the MCL when compared to wells with a nitrate concentration below the MCL. Compost N applications are 5 lbs/acre lower. The nitrate concentration in groundwater pumped for irrigation is used to calculate N applied via groundwater irrigation. At the average rate of groundwater irrigation reported by growers (2 ft/acre), a nitrate concentration of 10 mg/L adds 54 lbs/acre to the total N application. Here, the mean nitrate concentration in the subset of wells with a nitrate concentration above the MCL is 29 mg/L higher than in the “below the MCL” subset which leads to a higher N application of approximately 150 lbs/acre in the “above the MCL”. This difference alone does not imply that high nitrate concentrations in groundwater used for irrigation are the direct cause of high nitrate concentrations leaching into groundwater. However, this “irrigation” N application accounts for 75% of the difference in total N application between the two groups (194 lbs/acre). This indicates that nitrate in groundwater used for irrigation is not sufficiently accounted for in nitrogen application rates.

4.1.2 Recharge and Groundwater Age

We find no significant difference between the $^3\text{H}/^3\text{He}$ ages between wells with nitrate concentrations above or below the MCL. This is in line with our previous finding that there is no trend with age in the proportion of wells with nitrate above the MCL. It should be noted that the $^3\text{H}/^3\text{He}$ age does not include vadose zone travel times and transport processes. To determine the relative importance of travel times in the unsaturated and saturated zones for the delay of nitrate reduction measures requires a suite of environmental age tracers ($^3\text{H}/^3\text{He}$, ^{85}Kr , ^{39}Ar , ^4He) which was beyond the scope of this study.⁶⁰

We find stronger vertical age gradients in wells with nitrate concentrations above the MCL suggesting that downward groundwater flow, possibly accelerated by deep pumping, increase the potential for high nitrate concentrations to reach the aquifer depths where groundwater is extracted. Shallower water tables further contribute to more efficient pathways for nitrate to leach down to groundwater.

Finally, we find slightly higher recharge temperatures and subtly higher $\delta^{18}\text{O}$ values. These two results can indicate a smaller contribution of direct river recharge and a larger contribution of recharge from natural precipitation or irrigation.

4.1.3 Denitrification

The mean dissolved oxygen concentration is higher and the mean fraction denitrified is lower in the subset of samples with a nitrate concentration above the MCL. The difference in model groundwater age indicates that high nitrate concentrations are more prevalent in modern groundwater.

Table 12. t-test of explanatory variables.

Characteristic	Number of samples with data on characteristic		Mean value of characteristic in each group		Difference in mean values	Significance level (p-value)
	$\text{NO}_3\text{-N} < \text{MCL}$	$\text{NO}_3\text{-N} > \text{MCL}$	$\text{NO}_3\text{-N} < \text{MCL}$	$\text{NO}_3\text{-N} > \text{MCL}$		
$\text{NO}_3\text{-N}$ (mg/L)	4627	1855	2.6	31.2	29	< 0.001
fertilizer N (lbs/acre)	800	660	318	352	34	< 0.001
soil N (lbs/acre)	800	660	65	81	17	< 0.001
irrigation N (lbs/acre)	800	660	65	214	149	< 0.001
compost N (lbs/acre)	800	660	12	7	-5	< 0.01
total nitrogen application (lbs/acre)	800	660	460	654	194	< 0.001
dissolved oxygen (mg/L)	1240	710	3.7	5.4	1.7	< 0.001
fraction denitrified (-)	103	60	0.40	0.18	-0.2	< 0.001
$^3\text{H}/^3\text{He}$ age (years)	123	50	14	17	3	-
vertical age gradient (ft/yr)	4560	1844	6.5	8.7	2.2	< 0.001
depth to water table (ft)	4627	1855	121	78	-43	< 0.001
noble gas recharge temperature ($^{\circ}\text{C}$)	300	90	14.2	15.6	1.4	< 0.01
$\delta^{18}\text{O}$	370	103	-6.2	-6.0	0.2	< 0.05

4.2 Comparison of Nitrate Sources and Signature to Other Regions in California

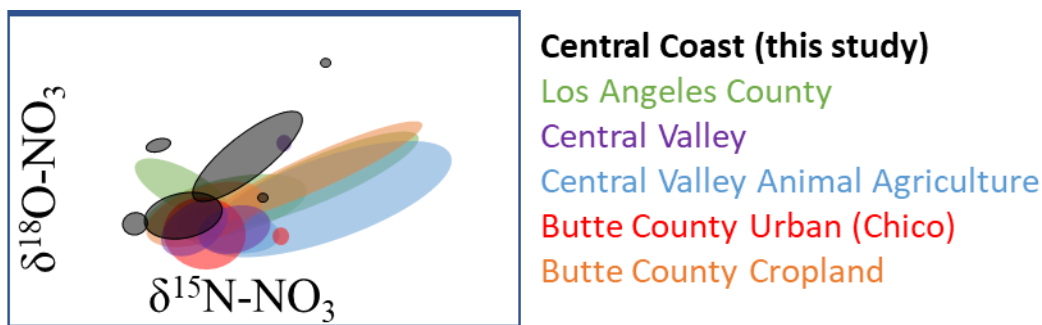


Figure 19: Comparison of nitrate isotopic data with other California regions.

Figure 19 illustrates the nitrate isotopes measured in Central Coast groundwater, relative to nitrate isotopes measured in other parts of California.²⁰ $\delta^{15}\text{N-NO}_3$ values are typically lower than other areas, reflecting a larger proportion of synthetic fertilizer and a smaller or absent contribution of manure. Typical values found at Central Valley animal agriculture areas with higher $\delta^{15}\text{N-NO}_3$ are not found in the Central Coast. $\delta^{18}\text{O-NO}_3$ values are higher than most other areas reflecting $\delta^{18}\text{O-NO}_3$ of coastal precipitation being incorporated in nitrate. Similarly high values are found in LA county, another coastal location. The denitrification trend in the Central Coast is steeper than elsewhere, possibly indicating slower two step denitrification involving N_2O (which has higher enrichment in oxygen isotopes than for nitrogen) and is likely under high rates of inorganic N application.⁶³

5 Conclusions

Nitrate concentrations are above the MCL in 29% of all groundwater samples in Central Coast groundwater basins. The proportions vary between Santa Maria Valley (35%), Salinas Valley (25%), and Gilroy-Hollister Valley (29%). The majority of these data is from the ILP monitoring efforts collected mainly between 2012 and 2017, with additional data from GAMA Priority Basin, GAMA Shallow Aquifer Assessment projects.

Groundwater ages were calculated from $^3\text{H}/^3\text{He}$ isotope ratios to study the history of nitrate loading to groundwater. Forty six percent of groundwater samples was “modern”: they had recharged since the 1950s and contained tritium but no evidence for fossil water. Twenty percent of samples were identified as fossil groundwater, recharged over a thousand years ago. An additional 19% of samples were a mixture between modern recharge and fossil water. Fifteen percent of samples had recharged entirely before 1950 (contained no detectable tritium and no $^3\text{H}/^3\text{He}$ could be calculated), but they also had no evidence of fossil water. The absence of the youngest groundwater makes it difficult to evaluate the effects of nutrient management plans. Dedicated first encounter monitoring wells and analysis of nitrate unsaturated zone cores can aid to the understanding of nitrate leaching in the Central Coast basins.

Groundwater age generally increases with depth below the water table. The age-depth gradient is spatially variable with high gradients in Santa Maria Valley and moderate gradients in the central part of the Salinas Valley. Low age gradients were found in the upper Salinas Valley.

Detailed data on Total Nitrogen Applied on agricultural land, reported by growers to the Irrigated Lands Program in 2018, were analyzed to evaluate the contribution of different sources to the present-day soil nitrogen budget. Fertilizer is the most prevalent source of nitrogen (63%) applied to agricultural lands. Fertilizer nitrogen is cycled through soil organic matter by microbial interactions or by plant uptake and subsequent composting of biomass. Fertilizer nitrogen has accumulated in agricultural soils and is available to plants at high concentrations, contributing 14% to the soil nitrogen budget. Nitrate in pumped groundwater used for irrigation is another important source of nitrogen to agricultural lands (22%). Where the total nitrogen application is above 1000 lbs/acre, this source can contribute up to 40% of total N applied.

Analysis of oxygen and nitrogen isotopes in groundwater nitrate can provide an indication of the original source of nitrogen leaching. However, biogeochemical cycling of nitrogen in soils often resets the nitrate isotopic signature before leaching to groundwater. Nitrate isotopes identify a direct fertilizer source of groundwater nitrate in six samples and a direct contribution of ammonia or urea fertilizer to groundwater nitrate in six samples. Two samples probably have a septic or manure source.

The proportion of wells with nitrate concentrations above the MCL are between 12% and 40% for all age categories except fossil groundwater. In six out of 73 samples (8%) that are classified as fossil groundwater, the nitrate concentration is above the MCL. Differences between modern groundwater age categories recharged since the 1950s are not significant. This indicates that high nitrate concentrations have leached into groundwater starting before the 1950s and continued into the 2000s. Long wells screens—over 50% of wells in this dataset has a screen length greater than 100 ft—cause mixing of groundwater flow paths and limit the ability to detect trends in response to changes in land management practices.

Low $\delta^{18}\text{O}$ values and low noble gas recharge temperatures in groundwater at the eastern side of Santa Maria Valley indicate river water is a source of recharge to the basin. Clear patterns in $\delta^{18}\text{O}$ or NGRT are not found in the Salinas Valley or Gilroy-Hollister Valley.

Nitrate concentrations are lower in groundwater with a river water recharge source than in groundwater recharged by local precipitation or groundwater-irrigation return flow. While river water recharge results in lower nitrate concentrations, 35% of wells still contain nitrate in excess of the MCL in areas of river water recharge as opposed to 70% in the remainder of Santa Maria Valley.

Without denitrification occurring in soils and groundwater, nitrate concentrations would exceed the MCL in more wells. We estimate that in 16% of all wells, the nitrate concentration is below the MCL because of denitrification. Nitrate concentrations still exceed the MCL in 29% of all samples.

Based on the dataset compiled for this study, wells with nitrate concentrations above the MCL have (1) higher N application rates from fertilizer, soil and irrigation, (2) higher vertical age gradients and shallower groundwater tables, (3) a smaller component of river recharge and a larger contribution of natural precipitation or irrigation recharge, and (4) higher dissolved oxygen concentrations and less denitrification.

6 References

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Table 13. Date, location, and well construction information of newly collected samples.

ID	Date m/d/y	Latitude °	Longitude °	Area	Depth ft	Top ft	Bottom ft
CCWB01	6/20/2018	35.00	-120.47	SMV			
CCWB02	6/20/2018	35.04	-120.55	SMV			
CCWB03	6/20/2018	35.20	-120.61	SMV			
CCWB04	12/4/2018	34.90	-120.39	SMV	699	480	219
CCWB05	12/11/2018	34.91	-120.46	SMV	950	279	328
CCWB06	12/11/2018	34.91	-120.46	SMV	966	291	216
CCWB07	12/11/2018	34.91	-120.47	SMV	870	310	
CCWB08	12/11/2018	34.96	-120.58	SMV			
CCWB09	12/11/2018	34.96	-120.51	SMV		380	
CCWB10	1/22/2019	36.85	-121.79	SV			
CCWB11	1/22/2019	36.69	-121.68	SV			
CCWB12	1/23/2019	34.90	-120.32	SMV			
CCWB13	1/23/2019	34.96	-120.57	SMV	240		
CCWB14	1/28/2019	35.11	-120.61	SMV		75	98
CCWB15	1/28/2019	35.04	-120.57	SMV		200	140
CCWB16	1/28/2019	35.11	-120.61	SMV		34	46
CCWB17	2/1/2019	34.94	-120.39	SMV	248		
CCWB18	3/4/2019	34.98	-120.51	SMV	200	100	
CCWB19	3/4/2019	35.01	-120.54	SMV	70		
CCWB20	3/4/2019	34.97	-120.51	SMV	70		
CCWB21	4/29/2019	36.19	-121.08	SV			
CCWB22	4/29/2019	36.11	-121.01	SV			
CCWB23	4/29/2019	36.41	-121.27	SV	160		
CCWB24	4/30/2019	36.30	-121.22	SV	600		
CCWB25	4/30/2019	36.60	-121.61	SV	190		
CCWB26	4/30/2019	36.33	-121.32	SV			
CCWB27	4/30/2019	36.01	-120.92	SV	300		
CCWB28	5/1/2019	36.49	-121.43	SV			

ID	Date m/d/y	Latitude °	Longitude °	Area	Depth ft	Top ft	Bottom ft
CCWB29	5/1/2019	36.45	-121.44	SV			
CCWB30	5/1/2019	36.51	-121.41	SV			
CCWB31	5/1/2019	36.64	-121.58	SV			
CCWB32	5/1/2019	36.63	-121.60	SV			
CCWB33	5/2/2019	36.67	-121.75	SV			
CCWB34	5/2/2019	36.86	-121.79	SV			
CCWB35	5/2/2019	36.61	-121.53	SV	500		
CCWB36	5/2/2019	36.61	-121.53	SV	800		
CCWB37	5/2/2019	36.78	-121.78	SV	1600		
CCWB38	5/3/2019	36.84	-121.78	SV			
CCWB39	5/3/2019	36.87	-121.69	SV			
CCWB40	5/3/2019	36.86	-121.69	SV			
CCWB41	8/19/2019	36.84	-121.48	GHV			
CCWB42	8/19/2019	36.85	-121.52	GHV	200		
CCWB43	8/19/2019	36.85	-121.49	GHV	420		
CCWB44	8/19/2019	36.85	-121.49	GHV	444	144	300
CCWB45	8/19/2019	36.85	-121.49	GHV			
CCWB46	8/20/2019	36.83	-121.43	GHV			
CCWB47	8/21/2019	36.87	-121.42	GHV	220		
CCWB48	8/21/2019	36.95	-121.45	GHV	300		
CCWB49	8/21/2019	36.88	-121.35	GHV	75		
CCWB50	8/22/2019	36.85	-121.47	GHV	220	100	100
CCWB51	8/22/2019	36.89	-121.42	GHV	140		
CCWB52	8/23/2019	36.84	-121.52	GHV			
CCWB53	8/23/2019	37.00	-121.52	GHV			
CCWB54	8/23/2019	36.95	-121.41	GHV	240		

Table 14. Results of new nitrate and isotope analyses.

ID	NO ₃ -N mg/L	$\delta^{15}\text{N}$ -NO ₃ ‰	$\delta^{18}\text{O}$ -NO ₃ ‰	$\delta^2\text{H}$ -H ₂ O ‰	$\delta^{18}\text{O}$ -H ₂ O ‰	³ H pCi/L
CCWB01	31.3	3.31	1.34	-38.54	-5.71	2.4
CCWB02	66.1	13.09	5.98	-37.53	-5.76	2.4
CCWB03	38.9	4.97	5.23	-33.08	-4.96	3.7
CCWB04	2.8			-46.68	-6.62	4.6
CCWB05	27.4	3.1	7.13	-45.72	-6.43	4.4
CCWB06	20.8	4.33	3.69	-45.41	-6.44	1.6
CCWB07	13.7	2.14	14.17	-47.56	-6.79	0.8
CCWB08	7	7.28	5.45	-48.92	-6.97	0.7
CCWB09	38	4.67	4.87	-44.09	-6.15	3.8
CCWB10	56.7	7	5.25	-37.25	-5.56	2.6
CCWB11	53.7	8.33	6.51	-40.2	-5.82	2.0
CCWB12	8.4	3.77	4.07	-46.37	-6.59	4.3
CCWB13	60.7	8.37	7.17	-41.13	-5.73	3.5
CCWB14	12.2	7.3	3.06	-34.05	-4.97	5.9
CCWB15	24.8	3.38	2.11	-41.12	-6.05	1.9
CCWB16	13.2	5.55	3.46	-34.29	-5.02	4.9
CCWB17	36.3	6.08	5.38	-42.51	-5.96	5.1
CCWB18	62.4	4.76	6.12	-40.82	-5.75	3.4
CCWB19	92.1	2.58	4.81	-38.25	-5.58	2.4
CCWB20	90.1	6.97	5.16	-42.13	-5.79	3.6
CCWB21	8.5	4.35	13.01	-33.02	-4.23	2.8
CCWB22	0.2	19.45	27.93	-31.22	-4.55	3.3
CCWB23	9.9	9.92	13.44	-34.15	-4.68	4.5
CCWB24	11.1	3.12	14.8	-32.06	-4.4	3.4
CCWB25	2.5	16.03	17.16	-34.52	-4.84	1.7
CCWB26	22.9	6.34	2.85	-46.49	-6.7	0.3
CCWB27	0.2	23.85	12.78	-27.93	-4.2	4.5
CCWB28	19.9	5.03	3.95	-39.37	-5.5	3.6

ID	NO ₃ -N	δ ¹⁵ N-NO ₃	δ ¹⁸ O-NO ₃	δ ² H-H ₂ O	δ ¹⁸ O-H ₂ O	³ H
	mg/L	‰	‰	‰	‰	pCi/L
CCWB29	5.4	9.02	9.16	-37.74	-5.43	4.1
CCWB30	5.2	6.57	0.38	-49.69	-6.9	0.3
CCWB31	2.1	6.02	8.37	-45.05	-6.63	0.4
CCWB32	8.4	9.04	17.99	-35.31	-4.95	3.1
CCWB33	32.1	3.51	13.28	-41.13	-5.8	3.3
CCWB34	54.1	4.62	1.99	-34.79	-5.29	2.7
CCWB35	30.8	4.44	1.03	-44.86	-6.77	0.5
CCWB36	0.9	5.38	-0.74	-47.84	-6.88	0.1
CCWB37	0			-51.02	-7.26	-0.1
CCWB38	39.3	4.71	2.92	-36.21	-5.31	3.3
CCWB39	21	5.24	2.3	-39.25	-5.69	2.4
CCWB40	20.5	7.36	9.88	-39.49	-5.86	-0.1
CCWB41	12.7	3.93	25.52	-46.81	-6.38	0.2
CCWB42	20.4	9.86	11.29	-43.53	-5.95	2.4
CCWB43	10.1	10.09	13.55	-44.66	-5.7	4.7
CCWB44	8.9	14.22	16.96	-44.54	-5.71	4.9
CCWB45	10.6	10.99	14.11	-43.68	-5.41	4.5
CCWB46	7.1	9.35	6.85	-44.44	-5.8	2.1
CCWB47	23	8.7	3.87	-43.06	-5.54	0.4
CCWB48	0			-52.08	-7.09	0.1
CCWB49	1.5	12.35	9.95	-46.78	-6.72	3.2
CCWB50	9.8	10.18	21.44	-46.19	-5.75	7.8
CCWB51	0			-57.61	-7.67	0.5
CCWB52	0.2	11.73	-3.3	-48.14	-6.79	0.2
CCWB53	34.9	10.18	-5.89	-40.13	-5.73	5.8
CCWB54	1.3	8.97	4.67	-44.18	-6.11	3.8

Table 15. Results of new dissolved noble gas and nitrogen gas analyses.

ID	$^3\text{He}/^4\text{He}$	^4He	Ne	Ar	Kr	Xe	N_2
	-	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$
	$\times 10^{-6}$	$\times 10^{-9}$	$\times 10^{-9}$	$\times 10^{-6}$	$\times 10^{-9}$	$\times 10^{-9}$	$\times 10^{-3}$
CCWB01	1.37	42.9	184	327	77.2	10.2	16.1
CCWB02	1.49	66.7	275	415	86.6	11.6	15.0
CCWB03	1.42	53.8	220	343	74.1	10.1	21.9
CCWB04	1.63	104.0	417	506	101.0	12.6	28.8
CCWB05	1.48	123.0	481	509	101.0	12.3	29.7
CCWB06	1.43	85.7	331	420	87.2	11.4	22.9
CCWB07	1.42	86.6	354	443	93.2	12.2	24.1
CCWB08	1.41	82.8	333	428	90.1	11.8	22.9
CCWB09	1.47	114.0	464	534	107.0	13.0	31.9
CCWB10	1.66	56.7	266	383	79.1	10.5	19.5
CCWB11	1.40	91.4	371	551	117.0	14.8	31.7
CCWB12	1.35	64.8	278	450	101.0	14.3	21.3
CCWB13	1.49	59.7	255	375	81.7	10.8	34.3
CCWB14	1.46	58.9	250	375	82.1	10.9	18.6
CCWB15	1.46	54.4	236	349	77.3	10.4	18.1
CCWB16	1.40	51.0	217	340	75.0	10.3	15.6
CCWB17	1.37	49.9	233	385	86.9	11.6	19.3
CCWB18	0.20	4490.0	290	391	84.4	10.4	22.1
CCWB19	0.97	350.0	816	685	118.0	13.1	50.3
CCWB20	1.43	63.6	257	361	79.6	10.2	19.6
CCWB21	0.90	543.0	205	360	81.6	10.9	21.0
CCWB22	0.59	421.0	238	343	77.7	10.0	37.9
CCWB23	1.08	84.6	268	376	81.7	10.5	24.8
CCWB24	1.50	58.9	243	352	77.1	10.1	17.3
CCWB25	1.43	71.4	299	422	91.8	11.7	27.3
CCWB26	1.36	75.6	329	474	98.0	12.6	23.4
CCWB27	1.38	47.2	204	334	77.4	10.4	15.2

ID	$^3\text{He}/^4\text{He}$	^4He	Ne	Ar	Kr	Xe	N_2
	-	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$	$\text{cm}^3\text{STP/g}$
	$\times 10^{-6}$	$\times 10^{-9}$	$\times 10^{-9}$	$\times 10^{-6}$	$\times 10^{-9}$	$\times 10^{-9}$	$\times 10^{-3}$
CCWB28	1.54	60.5	242	362	80.4	10.4	18.2
CCWB29	1.15	197.0	641	570	104.0	12.4	38.0
CCWB30	1.18	85.1	369	415	80.8	10.5	19.1
CCWB31	0.82	149.0	352	430	91.6	12.0	24.4
CCWB32	1.49	67.4	273	390	85.1	11.3	23.3
CCWB33	1.41	39.4	190	324	73.4	10.1	15.5
CCWB34	0.45	285.0	285	384	80.4	10.8	22.3
CCWB35	1.25	78.8	291	414	88.3	11.9	19.5
CCWB36	0.40	282.0	345	449	95.8	12.0	22.6
CCWB37	0.37	824.0	413	490	77.0	12.6	19.6
CCWB38	1.57	54.6	357	399	75.5	10.9	17.3
CCWB39	1.50	53.7	467	457	77.3	10.7	17.2
CCWB40	1.46	56.7	233	363	86.0	11.7	17.4
CCWB41	1.46	86.2	738	553	86.8	11.6	50.0
CCWB42	1.43	138.0	538	525	99.5	11.9	38.5
CCWB43	0.93	162.0	392	459	92.7	12.1	30.6
CCWB44	1.45	146.0	592	528	100.0	12.4	37.6
CCWB45	1.13	158.0	486	491	97.4	11.9	43.0
CCWB46	1.36	54.0	225	361	82.0	10.9	23.9
CCWB47	1.50	234.0	896	734	129.0	13.7	51.7
CCWB48	5.80	346.0	256	397	87.6	11.7	22.1
CCWB49	0.15	3370.0	261	383	84.7	10.8	21.7
CCWB50	1.41	95.6	391	426	85.1	10.4	29.8
CCWB51	5.73	871.0	375	460	96.3	12.9	25.7
CCWB52	0.51	226.0	332	422	90.3	11.6	25.8
CCWB53	1.49	83.4	345	435	89.6	11.4	26.1
CCWB54	6.31	505.0	379	434	88.1	11.6	29.0

Table 16. $^3\text{H}/^3\text{He}$ age, terrigenous helium, age category, noble gas recharge temperature (NGRT), and excess nitrogen gas.

ID	$^3\text{H}/^3\text{He}$ age years	Terrigenous Helium $\times 10^{-9} \text{ cm}^3 \text{ STP/g}$	Age Category -	NGRT $^{\circ}\text{C}$	$\text{N}_{2,\text{exc-N}}$ mg/L
CCWB01	3.7	0	modern	17.6	3.1
CCWB02	29.8	0	modern	13.4	1.2
CCWB03	12.2	0	modern	18.3	6.3
CCWB04	38.1	0	modern	11.8	4.9
CCWB05	27.4	0	modern	14.0	4.9
CCWB06	28.3	0	modern	15.5	4.9
CCWB07	37.5	0	old/unknown	13.1	3.5
CCWB08	32.4	0	old/unknown	14.0	4.0
CCWB09	28.0	0	modern	9.4	5.5
CCWB10	39.2	0	modern	17.1	2.9
CCWB11	18.2	0	modern	9.1	2.5
CCWB12	0.0	0	modern	7.7	3.6
CCWB13	23.9	0	modern	15.7	24.7
CCWB14	14.0	0	modern	15.4	4.1
CCWB15	27.7	0	modern	17.3	4.4
CCWB16	7.9	0	modern	17.6	2.5
CCWB17	1.8	0	modern	13.3	4.2
CCWB18		4420	mixed	17.2	4.4
CCWB19		120	mixed	16.8	6.7
CCWB20	14.8	0	modern	17.9	5.9
CCWB21		494	mixed	14.8	8.2
CCWB22		362	mixed	18.6	28.9
CCWB23		16	mixed	17.1	9.7
CCWB24	24.7	0	modern	18.1	3.1
CCWB25	24.5	0	modern	12.9	10.3
CCWB26		0	old/unknown	13.9	0.0
CCWB27	3.4	0	modern	16.9	2.1
CCWB28	27.5	0	modern	16.9	3.7

ID	$^3\text{H}/^4\text{He}$ age years	Terrigenous Helium $\times 10^{-9} \text{ cm}^3 \text{ STP/g}$	Age Category -	NGRT $^{\circ}\text{C}$	$\text{N}_{2,\text{exc}}\text{-N}$ mg/L
CCWB29		20	mixed	17.1	4.1
CCWB30		0	old/unknown	19.7	0.0
CCWB31		58	fossil	14.4	29.5
CCWB32	26.6	0	modern	14.8	9.0
CCWB33	11.2	0	modern	18.1	4.2
CCWB34		212	mixed	17.1	0.5
CCWB35		2	old/unknown	14.0	0.0
CCWB36		193	fossil	13.1	3.4
CCWB37		714	fossil	12.8	0.0
CCWB38	29.7	0	modern	20.0	0.0
CCWB39	28.4	0	modern	20.4	0.0
CCWB40		0	old/unknown	14.2	2.5
CCWB41		0	old/unknown	32.4	21.0
CCWB42	27.6	0	modern	16.0	15.0
CCWB43		58	mixed	14.5	11.6
CCWB44	23.6	0	modern	16.1	9.1
CCWB45		27	mixed	16.2	19.6
CCWB46	0.0	0	modern	15.4	10.6
CCWB47		0	old/unknown	15.6	7.3
CCWB48		283	fossil	13.3	5.0
CCWB49		3302	mixed	15.7	6.6
CCWB50	7.6	0	modern	18.4	10.9
CCWB51		773	fossil	12.4	5.0
CCWB52		141	fossil	14.9	6.7
CCWB53	21.1	0	modern	14.5	5.2
CCWB54		406	mixed	16.3	7.7